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A review on electrospun bio-based polymers for water treatment

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Abstract. Over the past decades, electrospinning of biopolymers down to nanoscale garnered much interest to address most of the millennia issues related to water treatment. The fabrication of these nanostructured membranes added a new dimension to the current nanotechnologies where a wide range of materials can be processed to their nanosize. Electrospinning is a simple and versatile technique to fabricate unique nanostructured membranes with fascinating properties for a wide spectrum of applications such as filtration and others. These nanostructured membranes, fabricated by electrospinning, were found to be of a paramount importance because of their advanced inherited properties such as large surface-to-volume ratio, as well as tuneable porosity, stability, and high permeability. The extensive research conducted on these materials extended the success of electrospinning not only to bio-based polymer nanofibres, but to their hybrids and their derivatives. The technique also created avenues for advanced and massive production of nanofibres. This paper reviews the recent developments in the electrospinning technique. Electrospinning of biopolymers, their blends and functionalization using metals/metal oxides, and the potential applications of electrospun nanofibrous membranes in water filtration are discussed.

Keywords: *nanomaterials, electrospinning, nanofibre materials, biopolymers, biocomposites*

1. Introduction

The exponential growth of the population, water scarcity, and man undesirable practices have spurred efforts to develop innovative technologies to produce high quality water at relatively low cost and energy [1, 2]. Urbanization, industrial activities, waste dumping, and alien plants are common practices contributing to the current environmental crisis [3, 4]. For example, the mining industries, although serving as a one of the driving forces of many countries' economy, dump billions of tons of hazardous materials into the environment. The emissions of such pollutants into the air and water are seriously considered as primary factors to the common respiratory, neural

and intestinal diseases. A safe and healthy environment is a priority that needs immediate intervention in both developing and well-developed countries [5, 6]. These challenges call upon novel and effective technologies to address the current environmental issues, either by protecting the environment and current water sources or by producing high quality water from available sources (oceans and wastewater) without harmful by-products [5, 6].

Over the past decades, the production of nanofibres gained much interest and attention to develop innovative materials with properties that are suitable to address the challenges related to water treatment. Nanofibres are a new class of nanomaterials with

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inherited properties such as the large surface-to-area ratio, high porosity, flexibility, stability, and permeability. Several routes have been utilized to fabricate these nanostructured materials from different materials such as drawing, templates synthesis, phase separation, self-assembly, electrospinning etc. [8–10]. Amongst them, electrospinning technique received a considerable interest due to its simplicity, efficiency and versatility in producing nanofibres [8–10].

In the electrospinning process, an electric field is introduced to the solution (or melt) to produce extremely long fibres with diameters down to a few nanometers. Almost all soluble materials can be electrospun into nanofibres. These include synthetic and natural polymers, polymer alloys and polymers loaded with chromophores, nanoparticles, or active agents, as well as metals and ceramics [8]. This technique gained much interest in the past two decades not only because of its simplicity, but also due to its feasibility to produce consistent long nanofibres with desirable properties which cannot be fabricated through other techniques. The resulting nanostructured materials with an extremely large surface to volume ratio, and engineered porosity, malleability, stability and functionality, have been applied in a wide variety of fields [8, 10].

Research has escalated in electrospinning of biopolymers, their hybrids and derivatives, for various applications because of their unique properties such as renewability, biodegradability and their abundant availability [7, 11]. Generally, biopolymers are defined as polymeric biomolecules generated by living organisms. They are categorized according to the monomeric units that build up the complex polymeric structure, namely polynucleids (ribonucleic acid (RNA) and deoxyribonucleic acid (DNA)), polypeptides (proteins), and polysaccharides (cellulose, and chitosan). The electrospinnability of most biopolymers is still a challenge because of numerous factors [11–15]. These include their rigid structure, high conductivity, high surface tension, and their gelation at fairly low concentrations. Several routes have been proposed to improve their electrospinnability such as the use of copolymers [16] and the modification of the processing device [13, 15].

A number of biopolymers, such as DNA [17], silk [18], chitosan [19], collagen [20], fibrinogen [21], gelatin [22], hyaluronic [13, 15], cellulose [23], and alginate [24] were successfully electrospun into nanofibres for their application in various fields such as

filtration, biomedical and tissue engineering. Only few of them were, however, applied in air and water treatment [25–27]. Their readily water solubility and biodegradation are common factors that disrupt the success of electrospun bio-based nanofibrous membranes, especially in water filtration. The addition of nanoparticles [28, 29], functionalization and the use of co-polymers [30] to enhance stability and biocidal activity have been the major object of research in electrospun nanofibrous membranes (ENM).

Even though there is some success in electrospinning a broad spectrum of materials since its invention a century ago, the throughput of nanofibres is still a limiting factor in the industrial production for commercial practice. However, there were several modifications on the classical laboratory electrospinning setup and new technological innovations to increase the production rate of the electrospun nanofibres. These technologies include bubble electrospinning [31], multi-jet [32] and bowl electrospinning [33].

In this review we discuss the fabrication of electrospun biobased nanofibres, their hybrids and derivatives using electrospinning technique. The factors that influence the properties of the electrospun nanofibres, and their functionalization using various methods, to enhance their performance in water and wastewater treatment, are discussed. We also look at other innovative technologies to modify classic electrospinning and to improve the properties and production of electrospun nanofibres.

2. Electrospinning process

2.1. Historical background on electrospinning

Electrospinning was initially not considered a viable technique because of difficulties with drying and collection of the nanofibres during its execution. However, it gained scientific and commercial publicity in the past two decades. Raleigh was the first to discover electrospinning in 1897, and a thorough study on electrospraying was done by Zeleny in 1914 [34, 35]. Cooley [36] was one of the scientists that patented the electrospinning technique about 100 years ago. However, the electrospinning technique gained enormous interest later in the early 1990s, thanks to the Reneker group. The group studied the mechanisms involved during electrospinning which spurred much interest in the nanotechnology arena because of the size of the resulting nanofibres. In Germany (in the early 1930s to 1940s), Formhals published a series

of patents based on the process and apparatus to execute this simple and versatile technique [37–39]. Later in the 1960s, Taylor studied the initiation of the jet from the drop on the apex of the needle when an electric field was applied. The conical shape formed because of the electric forces surmounting the solution surface tension was later named after him, ‘Taylor cone’ [10, 40]. By that time the technique was called ‘*electrostatic spinning*’. The considerable interest in the electrospinning technique in the 1990s resulted in the new name ‘*electrospinning*’ [40, 41]. The name ‘*electrospinning*’ was then accepted and is now widely used in the literature as a description of this viable technique to produce ultrathin fibres from a polymer solution or melt through application of electrical forces. The success of this technique is evidenced by the number of publications each year by universities, research institutes, and about 20 commercial enterprises, who are involved in the application of electrospun nanofibres (Donalson company Inc., Espin technologies Inc., and Elmarco etc.) [31].

2.2. Fundamentals of electrospinning

Almost all soluble materials can be electrospun into nanofibres, with diameters ranging from several micrometres down to tens of nanometres. Over 200 polymers were successfully electrospun into long ultrathin fibres for a wide variety of applications, mostly from polymer solutions [40, 42]. A classical setup of the electrospinning technique is shown in Figure 1. It consists of a spinneret with a metallic needle, a syringe pump, a high voltage power supply, and a grounded collector [8, 40, 43]. Horizontal and vertical setups are commonly adapted configurations, but in some cases upward electrospinning was also utilized [44].

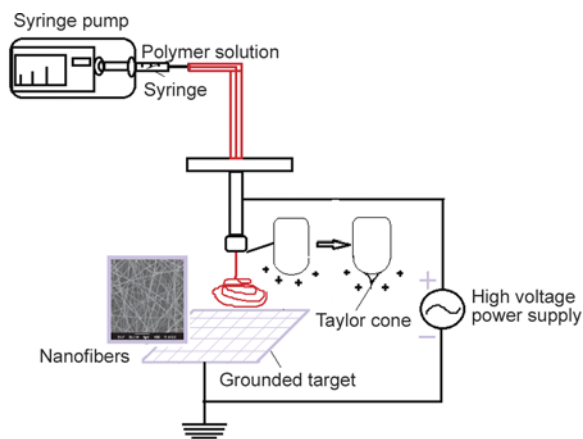


Figure 1. Schematic representation of electrospinning apparatus

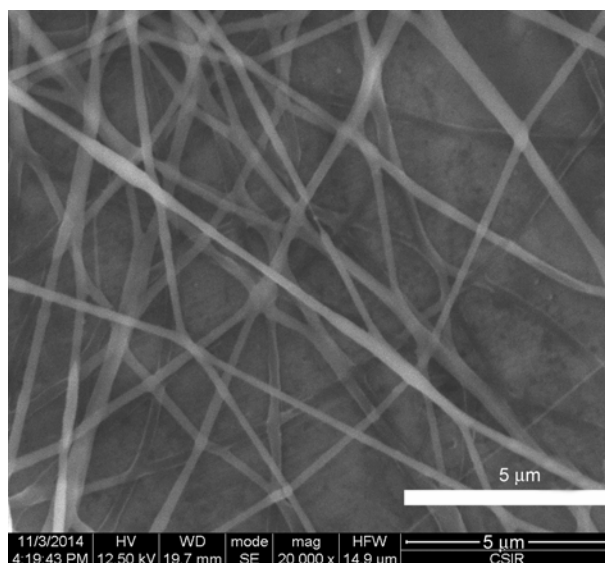


Figure 2. SEM micrograph of alginate nanofibres

Basically, the sol-gel, blend, composite, or polymer solution/melt is loaded in the syringe is driven to the needle tip by a syringe pump, forming a hemispherical droplet at the tip. A voltage (5–40 kV) is applied to the solution on the needle which causes the drop to stretch into a conical shape (known as Taylor cone) [45]. Depending on the viscosity of the solution (which must be sufficient enough to withstand stretching and whipping to avoid any varicose breakup, which forms nanoparticles) an electrified jet is formed and moves towards to an oppositely charged collector. During this trip the solvent evaporates and the jet solidifies to form nonwoven webs on the collector. The jet is only stable from the tip of the needle, whereafter instability starts. Interestingly, this technique offers the processor a platform to control the resulting morphology and structure of the nanofibres through changing of solution properties and physical parameters. Many well-organized papers describe in detail the effect of these parameters [8, 34, 43, 45]. Furthermore, the solvent and co-solvent play a significant effect in determining the resulting morphology and structure. The resulting nanofibres have high porosity, large surface to volume ratio, and good mechanical properties, which open doors for a wide variety (Figure 2) [8, 46].

3. Factors affecting the electrospinning process

Although electrospinning is a simple and straightforward technique, there are several parameters that are important (solution properties, processing parameters, and ambient conditions), that must be consid-

ered since they significantly affect the quality of the resulting nanofibrous membranes. The solution properties include conductivity, concentration, surface tension, and molecular weight; the processing parameters include voltage, tip-to-collector distance, collector shape, diameter of the needle and feeding rate; the ambient conditions such as humidity and temperature of the surroundings are also important.

3.1. Solution parameters

Despite the fact that all these parameters have a significant effect on the resulting product, the solution properties serve as a more decisive parameter. The solution concentration and/or viscosity have to be sufficient enough to prevent the varicose breakup of jet to allow a continuous stream in the spinning solution. Both are directly dependent on the polymer molecular weight which defines the entanglement of the chains to withstand the Coulombic stretching force to prevent the jet breakage into droplets by surface tension [47–50]. The optimal concentration and/or viscosity are required because too high concentration/viscosity may result in larger diameter and clogging of the capillary [47–50]. Nevertheless, the gelation (highly viscous) at fairly low concentrations (below entanglement concentration) disrupts the electrospinnability of the biopolymers, resulting in collection of droplets. Moreover, most of these polymers are inherently polyelectrolytic (e.g. alginate and chitosan) which increases the solution conductivity. This also contributes to the difficulties in electrospinning of natural polymers from their aqueous solutions [47, 51]. Several modifications have been done

to improve their spinnability. The use of copolymers such as poly(vinyl alcohol) (PVA) and polyethylene oxide (PEO) was found to be suitable to reduce the conductivity of the natural polymeric spinning solutions [47, 52–54].

On the other hand, some solvents may be added either to increase [55, 56] or decrease the electric properties of the spinning solution [12, 19]. The most used solvents in electrospinning are shown in Table 1.

Solvents with good volatility, moderate vapour pressure, moderate boiling point, good conductivity and good cohesion with the polymer is important in the electrospinning process [12, 56–61]. The solubility of the polymer, however, does not guarantee the solution spinnability [12]. For example, partial solubility in a solvent can result in smooth bead-free nanofibres. Some reports suggested that a single solvent system could result in beaded nanofibres, whereas the addition of partially soluble solvent could improve the nanofibre morphology [57, 59, 61].

3.2. Setup parameters

Essentially, the electrospinning process begin directly at the point at which electrostatic forces overcomes the solution surface tension and viscoelastic forces. Typically, a critical voltage is required to eject the charged jet from the drop at the nozzle (Taylor cone) [15, 62]. For instance as the concentration, or similarly, the viscosity increases, higher electrical forces are required to overcome both the surface tension and the viscoelastic forces for fibre stretching. The size of the droplet at tip of the nozzle depends on

Table 1. Properties of solvents and liquids used in electrospinning

Solvent	Density [g·cm ⁻³]	Viscosity [cP]	Boiling point [°C]	Dipole moment [D]	Dielectric constant	Surface tension [mN·m ⁻²]
Acetic acid	1.05	1.12	118.0	1.68	6.15	26.9
Acetone	1.39	0.32	78.0	2.88	27.0	21.4
Chloroform	1.50	0.53	61.6	1.15	4.80	26.5
Dichloromethane	1.33	0.41	40.0	1.60	8.93	28.1
Dimethylacetamide	0.94	1.96	165.0	3.72	37.8	36.7
Dimethylformamide	0.99	0.80	153.0	36.70	38.3	37.1
Dimethyl sulfoxide	1.10	2.00	189.0	3.90	46.7	43.0
Ethylene glycol	1.11	16.13	197.0	2.20	37.7	47.0
Formamide	1.13	3.30	211.0	3.37	110.	59.1
Formic acid	1.22	1.57	101.0	1.41	57.9	37.6
Glycerol	1.26	950	290.0	2.62	42.5	64.0
Hexafluoro isopropanol	1.60	1.02	58.2	1.85	16.7	16.1
Methanol	0.79	0.54	65.0	1.70	33.0	22.7
Tetrahydrofuran	0.89	0.46	66.0	1.75	7.52	26.4
Trifluoroethanol	1.38	1.24	74.0	2.52	8.55	43.3
Water	1.00	1.00	100.0	–	21.0	25.2

the feeding rate as well as the needle shape and diameter [13, 62–64]. Therefore, these factors influence the forces acting on the drop which contribute to the jet initiation and stretching. The optimal distance is required to give the electrified jet sufficient time for nanofibre dryness [65–67]. At longer tip-to-collector distance (TCD), the fibre will have sufficient time to solidify before reaching the collector, but if the distance is too long, either beaded fibres or no fibres are collected [65]. Similarly, when the distance is too short, it reduces the flight distance and solvent evaporation, and increases electric field, which results in beads.

One of the essential aspects in electrospinning is the type of collector used. These collectors act as a conductive substrate to collect the charged fibres. Aluminium foil [61] is usually used to collect the nanofibres. However, due to the difficulty to transfer the nanofibres from this collector [13, 15], other collectors such as liquid baths [68], metal plates [69], grids [70], parallel or gridded bars [71, 72], rotating disks [73], and rotating drums [74] were investigated as possible collectors. Different collectors used in electrospun nanofibres were recently reviewed in [46]. The collectors specifically used in electrospun biopolymers as well as the optimal conditions are summarized in Table 2. The collectors are often used to engineer and design the structure and morphology of the fibres. For example, Matthews *et al.* [75] observed that collagen nanofibres, collected at lower speeds, were random filaments, whereas collection at higher speeds resulted in deposition of the nanofibres along the rotation axis.

3.3. Ambient conditions

Ambient conditions, temperature and humidity, can also affect the morphology and diameter of the nanofibres [77]. It was deduced that the increase in temperature reduces the viscosity of the solution and enhances the solvent evaporation, which results in thinner nanofibres [89]. Depending on the system under investigation, two antagonistic effects are observed: (1) reduction in fibre diameters, and (2) increase in diameter which may result in fusion of the nanofibres [90]. Tripatanasuwan *et al.* [91] reported that an increase in relative humidity resulted in smaller diameters of the nanofibres. They stated that at the lower relative humidity the rate of solvent evaporation increased, with the opposite effect at higher humidity. Furthermore, the humidity can

generate pores of different size and depth depending on the molecular weight of the polymer [92].

4. Recent advances in electrospinning techniques

During the past years research on various advancements and modifications on standard needle electrospinning (SNE) with the aim to scale up the nanofibres production, to enhance the stability of the electrospinning technique, and to engineer patterns and desired morphologies of the resulting nanofibres for various applications, has escalated. The production rate has been one of the inhibiting factors for the commercial implementation and industrial viability of the electrospinning processing technique. In SNE the mass production rate is approximately $0.01\text{--}0.1\text{ g}\cdot\text{h}^{-1}$, where the nanofibre source is a single jet arising from a single needle apex through which the polymer solutions is ejected. Various innovative ways to produce electrospun nanofibres with enhanced functionalities were developed. These advances, namely multi-needle and needleless electrospinning, gas-jet electroblowing spinning, and coaxial electrospinning (Table 3) are described in the following sections. However, most of these technological advances are mostly applied in synthetic polymers as deliberated in Table 3.

4.1. Multi-needle electrospinning

An increase in the number of nozzles is the most convenient way to increase the production rate of the nanofibres [100, 101]. However, there are some drawbacks associated with multi-needle electrospinning, such as complicated design and large operating space, and repulsion between the nanofibres that causes the uneven deposition of the nanofibres [102]. Furthermore, the clogging of needles discourages the industrial viability of multijet spinning. In industry the needles would require regular cleaning, which would result in complex processes and too much labour. Therefore, several modifications were suggested to overcome the nanofibre repulsions without compromising the production rate. For example, Kim and Park [103] electrospun alginate/PEO nanofibres using multi-nozzle electrospinning with an extra auxiliary electrode to alleviate the repulsion between the jets. PEO (2 wt%)/alginate (2 wt%) doped with lecithin (0.7 wt%) as surfactant produced smooth nanofibres using SNE. The same composition was used for a comparison between nanofibres

Table 2. The optimal conditions of electrospun biopolymer nanofibres

Type of collector	Polymer system	Solvent system	Conditions	Morphology	Diameters	Reference
Aluminium foil	Cellulose ($DP = 210$)	NMMO/water	9 wt%, 15–20 kV, 15 cm, 0.05 mL·min ⁻¹	Film	–	[76]
	Alginate (37 kDa)/PEO (600 kDa)	Distilled water	Alginate-PEO-Pluronic (10:0:0.8:1.5 wt%), 12 cm, 0.5 mL·h ⁻¹ , 30% relative humidity (RH)	Three dimensional (3D)	237±33 nm	[77]
	Carbomethyl cellulose (CMC)/PEO (1:1 ratio)	1:1 water:ethanol	8%, 20 cm, 35 kV	Uniform	200–250 nm	[11]
	Hydroxypropyl methyl cellulose (HPMC) (with 29.2% methoxy and 8.8% hydroxypropoxy)	1:1 water:ethanol	2.14%, 20 cm, 35 kV	Uniform	128 nm	[11]
	Cellulose ($DP = 1140$)	LiCl/DMAc	3 wt%, 15–20 kV, 15 cm, 0.05 mL·min ⁻¹	Film	–	[76]
	Chitosan (106 kDa)	90% Acetic acid	7%, 3 kV·cm ⁻¹ , 20 μ L·min ⁻¹	Uniform	180 nm	[67]
	Chitosan	90% Acetic acid	5 wt% (hydrolyzed in 50% NaOH at 95°C for 48 hours), 16 cm, 17 kV, 8·10 ⁻² mg·h ⁻¹ , $ID = 0.7$ mm	Uniform	50–250 nm	[78]
		80% Acetic acid	7 wt%	Uniform	250±76 nm	[78]
	Chitosan ($DD = 85\%$)/agarose	70% Acetic acid	7.5 wt%	Uniform	284±94 nm	[78]
		TFA/DCM (7/3 v/v)	7% (50% of agarose), 15 kV, 12 cm, 0.5 mL·h ⁻¹	Cylindrical	0.14±0.09 μ m	[79]
	Chitosan (8–20 kDa)/PLA (5 kDa)	TFA	17.4 wt% (1.20 chitosan:PLA)	Uniform	–	[80]
	Carboxymethyl chitosan (89 kDa, 0.36 DS)/PVA (124–186 kDa, 87–89% hydrolysed)	Water	8% mixture of 60/40 (CMCS/PVA) with 0.5 Triton X100, 10–15 kV, 17–20 cm	Uniform	135 nm	[81]
	Hexanoyl chitosan	Chloroform	14 wt%, viscosity = 956 mPa·s, 1 kV·cm ⁻¹	Ribbon-like	3.93 μ m	[82]
	Quaternized chitosan(QCh)/PVP	Distilled water	20 wt%(QCh)/PVP (4:1), 2.2 kV·cm ⁻¹ , viscosity = 25 550 cP,	cylindrical	1.53±0.48 μ m	[83]
	PEG-N ₃ O-chitosan ($DS = 1.50$)	75/25 v/v (THF/DMF)	15% with 0.5 wt% Triton X100, 10–15 kV, 17–20 cm	Uniform	162 nm	[84]
	Gelatin	Distilled water	At 37°C, 14 cm, 13 kV	Beaded cylindrical	295 nm	[85]
Rotating mandrel	Gelatin	Formic acid	8 wt%, 7.5 cm, 1 kV·cm ⁻¹	smooth	79±14 nm	[66]
	Thiolated HA (158 kDa)/PEO (900 kDa)	Dulbecco's modified eagle's medium	HA-DTPH (2.5%, w/v)/PEO (2.5%, w/v), 20 μ L·min ⁻¹ , 10 cm, 18 kV	3D	90±15 nm	[86]
	N-carboxyethyl chitosan/PEO/AgNO ₃	Formic acid	37 kV, 14 cm, 800 rpm, 1.1 mL·h ⁻¹	Self-bundled/yarn	460±87 nm and 200±40 nm	[87]
	Collagen (calf skin type 1)	HFIP	0.083 g·mL ⁻¹ , 25 kV, 125 mm, 5.0 mL·h ⁻¹	3D	100±40 nm	[75]
Liquid bath	Ethyl cellulose	TFA	10 wt%, 20 kV, 5 cm, 0.01 mL·min ⁻¹	Uniform	100 nm	[88]
	Cellulose acetate (CA)(40 kDa)	DMAc/acetone(1/2)	10%, 15 cm, 20 kV	Uniform	420 nm	[29]
	Cellulose	1-butyl-3-methylimidazolium chloride	10% cellulose, 15 cm ethanol bath, 15–20 kV, 0.03–0.05 mL·min ⁻¹	Highly-branched	8.65±7.70 μ m	[14]
	Alginate (3500 cps)	Glycol/water (2/1)	2 w/v%, 28 kV, 12 cm, copper mesh in 10 wt% of CaCl ₂ in ethanol, 105 μ L·min ⁻¹	Uniform	200 nm	[12]
Rotating collector immersed in liquid bath	Cellulose ($DP = 210$)	NMMO/water	9 wt%, 15–20 kV, 15 cm, 0.01 mL·min ⁻¹ , 1.2 rpm, water bath	Uniform	300 nm and	[76]
	Cellulose ($DP = 1140$)	NMMO/water	2.5 wt%, 15–20 kV, 15 cm, 0.01 mL·min ⁻¹ , 1.2 rpm, water bath	Uniform	250–750 nm	[76]

Table 3. The novel advances on standard laboratory electrospinning

Technique	Polymer concentration [wt%]	Average diameter [nm] and voltage[kV]	Throughput [g·h ⁻¹]	Reference
Bowl	6 (PEO) and 12 (PCL)	268±25 at 16 and 344±97 at 30	7.0	[31]
Bubble	10 (PVA)	111–48.6 at 10–30	–	[33]
Conical wire coil	9 (PVA)	275±113 at 50	2.8	[93, 94]
Gas jet	8 (PVA)	220 at 25	1.1	[95]
Multi-jet	15 (PVA)	230000	0.66–0.72	[96]
Nanospider	15 (PU)	193 at 81.2	96.6 ^a	[97]
Porous tubular	20 (nylon-6)	170.6±5.0 at 20	5.0	[98]
Splashing	9 (PEO)	368±45.37 at 60	3.0	[99]

^aUnits g·h⁻¹·m⁻¹

produced with and without auxiliary electrodes in multi-nozzle spinning. The auxiliary supported multi-nozzle showed a higher production rate and smoother nanofibres with diameters of 174±62 nm compared to unsupported spun nanofibres that had diameters of 246±62 nm. A wide variety of multijet electrospinning heads, namely series, elliptic, concentric, line, rectangular and matrix can be utilized to produce nanofibres [96]. The biodegradable blend of cellulose acetate and PVA was prepared by varying the ratio of the jets from 1:3 to 3:1. The average diameters of the fibres increased (220 to 290 nm) with a decrease in the number ratio of PVA/CA from 3:1 to 1:3. The tensile strength and the modulus increased from 7.0 to 9.4 MPa and 18.1 to 34.0 MPa with an increasing the number ratio of the jets of PVA/CA from 1:3 to 3:1 [26].

4.2. Needleless electrospinning

4.2.1. Confined needleless electrospinning

One of the promising processes to scale-up the nanofibre production is needleless electrospinning. This technique avoids the issues of clogging and cleaning of the needles and the complexity of the multi-axial spinning setup. The needleless process is divided into two categories depending on the feeding system: confined feeding and unconfined feeding. The difference between the confined and unconfined needleless electrospinning is the fact that in confined electrospinning the electrospun fluid is enclosed in a reservoir such as an insulating tube [98, 104, 105] or any other material in which the polymer is protruded, whereas in unconfined systems there is no reservoir for the spinning solution and the droplets are projected naturally from the surface of the solution.

The replacement of the needles in multi-jet spinning is the most convenient way to resolve the complexity and difficulties without compromising the

mass throughput [92, 99]. In this route the polymer fills a porous hollow tube [93, 104]. The drilled holes on the surface of the tube can be made in different configurations. The positive electrode is immersed into the solution and by using a small pressure the polymer solution is driven through the holes. The production rate is 3–250 times that of the standard electrospinning (SNE), while the nanofibre diameters may range from 300 nm to several hundreds of microns. Dosunmu *et al.* [98] used a porous polyethylene tube with pore sizes 10–100 µm as reservoir for a 20 wt% nylon 6 spinning solution. The polymer solution was pushed with air pressure to form multiple jets on the porous surface. The jets protruding from the tube surface were collected on a surrounding vertically placed grounded co-axial wire mesh. The resulting nanofibres have equivalent mean diameters to those produced by SNE, with a much broader distribution. Moreover, different polymers can be electrospun via this method and the porous tube can be made from different materials such as ceramic.

Rotary-jet spinning (RJS) is composed of a rotating motor, a reservoir and a stationary or rotating collector [106]. The polymer solution is loaded into a punched reservoir, either continuously or once in one measurement or production. The perforated reservoir has two side wall orifices which rotate vertically to the surrounding collector. Because of the centrifugal forces on the solution, the polymer jets are forced out of the reservoir through the punched side wall, and subsequent jet extension and dryness yield three dimensions of nanofibres. The advantages include the use of low voltages, the production of three dimensional (3D) morphologies, controlled porosity, independence of solution conductivity, and larger mass production than SNE. Various polymer solutions (poly(lactic acid) (PLA) in chloroform, polyethylene oxide (PEO) in water,

poly(acrylic acid) (PAA) in water, gelatin in acetic acid were successfully electrospun to three dimensional nanofibres by Badrossamay *et al.* [106]. They indicated that with the control over the spinning solution concentration and rotating speed the morphology of the nanofibres can be tuned.

4.2.2. Unconfined needleless electrospinning

Unconfined needleless electrospinning is the electrospinning the solutions naturally from a liquid surface. Yarin and Zussman [107] prepared nanofibres by a needleless method using the ferromagnetic liquid sub-layer below the polymer solution. It was established that the nanofibres can also be produced without a ferromagnetic sub-layer, but at a much higher voltage. The disadvantage of this method is that the number of jets and their location cannot be controlled since the jets protrude naturally from the liquid surface. Nevertheless, they produced nanofibres with diameters ranging from 200 to 800 nm.

Another technique involves the use of charged cylindrical rotators dipped in the spinning solution [108, 109]. This is the only technique that was applied industrially since research on the enhancement of the production rate started, and is known as nanospider™ [97]. The technique involves a polymer solution in a container and a cylindrical charged metal rotating at a certain speed. The charged rotating metal is partially immersed in the solution. When the solution is electrified by the voltage supplied to the cylindrical rotators, the multiple polymer jets are launched from the circumference of the cylindrical rotators to the grounded collector. Nanofibres with average diameters between 50 and 200 nm are produced at a rate of $2.53 \text{ g}\cdot\text{h}^{-1}$, compared to conventional electrospinning with a rate of $0.01\text{--}0.1 \text{ g}\cdot\text{h}^{-1}$. Various shapes of rotating nozzles, such as disk and spiral coils, can be used to generate narrow distribution nanofibres with a higher mass production than SNE. A rotating spiral coil made of metal wire was used by Wang *et al.* [94] to eject the jets from the surface of each spiral wire. Depending on the concentration and applied voltage, ultrafine nanofibres were produced. Nanofibres with narrower distribution were generated with the mass production increasing with voltage from 2.94 to $9.42 \text{ g}\cdot\text{h}^{-1}$ for 45 and 60 kV, respectively. The disadvantage of these nozzle processes is the uneven electric field distribution on the spiral wire. Niu *et al.* [110] com-

pared a rotating disk and cylinder to envisage the effect of the shape on the resulting nanofibre production. They indicated that the disk nozzle requires a lower voltage to initiate the fibre production than the cylinder nozzle, with finer nanofibre than those from the cylinder at similar conditions. The mass production was equivalent for both the rotating disk and cylinder, but higher than that of SNE.

Another approach is the polymer solution dripping from the reservoir onto a rotating cylinder, known as splashing electrospinning. In this case the reservoir is held horizontal to a charged cylinder rotating at a certain speed. With a controlled speed, gap distance, and solution parameters the nanofibre structure can be tuned with enhanced production (24–45 times) compared to SNE [99] (Table 3). The influence of processing and solution properties on the resulting nanofibres via splashing was studied by Tang *et al.* [111]. Increased concentration was found to increase the mean diameter of the fibre, whereas an increase in the voltage decreased it. A decrease in mean diameter was reported with an increase in both rotating speed and gap distance. They found that using statistical analysis (analysis of variance (ANOVA)), the optimal conditions for fine nanofibres with narrower distribution (PEO in water) were as follows: concentration (6.94 wt%), voltage (12.38 kV), gap distance (3.5 cm), and rotational speed (0.76 rpm). Also, nanofibres with mean diameters ranging from 100 to 400 nm, were obtained.

In the bowl-edge unconfined process, the primary interaction between the electric field and the polymer solution caused fluid perturbations within the bath reservoir filled with polymer solution [31, 41]. These fluid perturbations were responsible for Raleigh-Taylor instabilities formed by gravity forces in the polymer solution. The polymer solutions, due to the instabilities, produced jets protruding from the edge of the bowl which are similar to the jets ejected from the SNE. The bowl has a thin-lipped edged structure where the droplets are ejected to the concentric collector. At the beginning, a high voltage is supplied and then the voltage to initiate the jet formation is reduced to a lower operational value. Stable nanofibres are formed on the collector with high quality nanofibres similar to the optimal nanofibres from SNE, with 40 times faster production. Bubble electrospinning is primarily based on the bubbles on the surfaces of polymer solutions [28]. These bubbles serve as the droplets in which the

Taylor cone is formed. The gas tube and metal electrode are inserted in the solution to produce the bubbles. When the gas is blown into the solution, the bubbles are formed (in a spherical shape) on the surface of the solution, and when the voltage is applied the bubble shape changes into a conical shape. When the voltage is above a critical value, multiple jets are ejected from the bursting bubble to the collector, while new bubbles are formed and broken again – the process repeats itself until the solution is depleted.

Another process necessitates the drops of a polymer solution dripped onto a standard spin coater followed by rotation of the chuck [112]. The fibres are produced by the instability of the spin-coated liquid that results from the competition of the centrifugal force and the Laplace force induced by the surface curvature. By adjusting the solution parameters (concentration, spinning speed, surface tension) and solvent evaporation rate, different polymers can be processed to their nanofibres. Dabirian *et al.* [113] modified the centrifugal spinning method by enclosing a nozzle to avoid the influence of the surrounding air on the dryness of the protruding polymer solution. They also applied a voltage which was not applied in the centrifugal spinning proposed by Weitz *et al.* [112]. They obtained uniform aligned nanofibres with an average diameter of 440 ± 11.3 nm. The mechanical properties of the resulting nanofibres were significantly improved compared to those of the electrospun nanofibres from SNE.

Yet another proposed electrospinning process necessitates the use of one or more plates held at a certain angle with respect to the horizontal and vertical oriented collector [114]. The reservoir on top of the plates drops the polymer solution onto the metal plate (which serves as a spinneret), and because of the angle and gravitational force the solution slowly flows until reaching the edge of the plate. At this point, the solution forms a drop that changes its shape to Taylor cone as a result of the electric field at the edge of the plate. More plates were used, given a ‘*waterfall geometry*’. However, the plates resulted in an irregular spinning due to the electric field difference and the polymer solution on each of the plates. The *waterfall geometry* process displayed lower production rate than the SNE and single edge-plate geometry. The advantage of the single plate method lies in its simplicity and ease of operation with a large number of jets ejected from the plate edge.

The disadvantage is the inhomogeneous electric field distribution in the solution, which contributes to the nanofibre structures.

Another needleless setup involves concurrently provoking numerous jets from a sufficiently large liquid surface [115]. The electrospinning is carried out on the free liquid surface with a stainless steel cleft with a certain width. Numerous jets are generated on the surface of the conductive liquid when sufficient voltage is applied. Mathematical equations were proposed and found to be well applicable to SNE and to most of the theories based on this processing technique. The hypothesis from different parameters and dimensionless analysis created a comprehensive description which affords the opportunity for the development of the liquid surface technique.

Nanofibres were also synthesized from conical wire coils as a spinneret [94]. The technique involves a copper wire-coil nozzle with a conical shape with a certain distance between the wires connected to the voltage supply. This technique falls in between the confined and unconfined, because the dripping solution is inside the cone held upside-down, while the reservoir is not enclosed since the droplets are ejected from the solution flowing through the space (gaps) between the wires. The flowing solution is exposed to a high voltage (40–70 kV) to produce the jets which travel towards the collector where the nanofibres are collected.

4.3. Gas-jet electrospinning

One of the recent advances includes new designs of the needle to fabricate the desired morphology and patterns for various applications. It necessitates a gas jet device connected to the needle and is known as the gas-jet electrospinning technique [13, 15, 116–118]. In this technique the needle of the spinning solution is encircled by the tube of the gas jet. Lin *et al.* [116] studied the effect of ID and gas flow rate while keeping the other parameters fixed. They found that a smaller ID led to smaller average diameters, while the average diameter decreased monotonically as the gas flow rate increased. It was suggested that the blown gas imposes an additional drawing action on the polymer jet. Other groups used hot stream air-blowing to control the solution properties, solvent dryness and to impose additional stretching to the jet [13, 15]. The blown air is heated by passing through heating elements offering con-

trol over the rate and temperature of the blown air. The tip-to-collector distance is much shorter than conventional electrospinning with very high voltages (~ 40 kV). The method offers an opportunity to increase the processing window boundaries. Ultra-high molecular weight polymers, and polymers that are difficult or impossible to electrospin from their aqueous solutions, can easily be electrospun through a gas jet process [13, 15, 86]. However, the throughput is still equivalent to that of SNE, while the diameters of the nanofibres range between 500 and 1000 nm. The disadvantage of this process is the difficulty of solvent recovery. An increase in the throughput will also require an increase in the number of the needles as well as large gas volumes [118].

Another gas jet process necessitates the exploitation of the protruding jet by applying compressed air to further stretch the jet [119, 120]. This process is known as gas jet nanofibre (GJF). The GJF consists of a syringe pump, modified nozzle, jet compressed gas (often air), and a collector. Several parameters, such as air jet pressure, feeding rate, and tip to collector distance, can be adjusted to engineer the nanofibres morphology. The mass production ranges between 0.9 and $8.6 \text{ g}\cdot\text{h}^{-1}$ depending on the polymer properties, solution parameters and processing parameters. However, bi-component and co-shell morphologies can easily be fabricated. Benavides *et al.* [120] produced nanofibres with average diameters of 280, 186 and 425 nm from 6% v/v PEO, 6% v/v poly(vinyl pyrrolidone) (PVP) and poly(vinyl acetate) (PVAc) using a 276 kPa compressed air jet with a feeding rate of $0.8 \text{ mL}\cdot\text{min}^{-1}$. They demonstrated that the nanofibre diameter can be reduced by increasing the air pressure. They also indicated that core-shell by co-axial syringe and side-by-side morphologies from immiscible polymers can easily be prepared.

4.4. Nozzle configurations for multi-component nanofibres

4.4.1. Co-electrospinning

The modifications of the standard electrospinning devices created a new avenue to combine one or more components with ease of functionalization. One of the simplest ways to fabricate one or more polymeric components is through the use of two or more needles containing different solutions (double electrospinning). This can be done by spinning both

solutions, fed from different reservoirs, in a programmed way such that both solutions reach the collector at the same time [121]. Another way is the depositing of the nanofibres in a sequential way, where one polymer solution is first deposited followed by the other [122]. In these methods the syringes filled with different polymers are placed opposite each other with the collector between them, and perpendicular to the principal axis of the collector. The ejected jets are collected using the same collector (mandrel). Nanofibrous membranes containing chitosan and alginate were produced *via* the dual-jet system by Hu and Yu [123]. The PEO/chitosan and PEO/alginate were fed from two different nozzles and the jetting difference was 15 seconds [123]. X-ray photon-electron spectroscopy (XPS) confirmed the compositions of the two biopolymers, and fluorescent microscopy micrographs showed that these polymers were evenly dispersed onto each other. A hybrid of chitin and silk fibroin (SF) were also electrospun simultaneously from their solutions fed from two syringes on opposite sides facing a rotating target [124]. Chitin/SF (75/25, 50/50, 25/75) hybrids were prepared from chitin (5 wt% in 1.1.1.3.3.3-hexafluoro-2-propanol (HFIP)) and SF (7 wt% in HFIP) and fed to two syringe in opposite directions. The resulting bimodal type of distribution consisted of thinner chitin nanofibres and thicker SF nanofibres with each component dominant depending on their concentration in the composition.

Similarly, the two polymer solutions in the syringes can be placed on opposite sides of the collector. The voltage applied to the syringes result in ejection of the jets which come into contact (merge into single nanofibres) moving towards the collector (Figure 3) [125]. Duan *et al.* [126] simultaneously electrospun poly(lactide-co-glycolide) (PLGA) and chitosan/poly(vinyl alcohol) (PVA) from different syringes and mixed them on the collector (drum). The solutions from the two syringes connected to a high voltage (15 kV) were fed by a double-way syringe pump at a feeding rate of $0.2 \text{ mL}\cdot\text{h}^{-1}$ to a grounded drum (TCP = 10 cm). The composite nanofibres with a diameter of 275 ± 175 nm consisted of both smooth nanofibres with large diameters and beaded nanofibres. Ji *et al.* [86] crosslinked hyaluronic acid (HA) hydrogel nanofibres by a primary syringe (2.5% w/v/2.5% w/v HA/PEO) connected to a T-shaped three-way steel adapter, and the secondary syringe

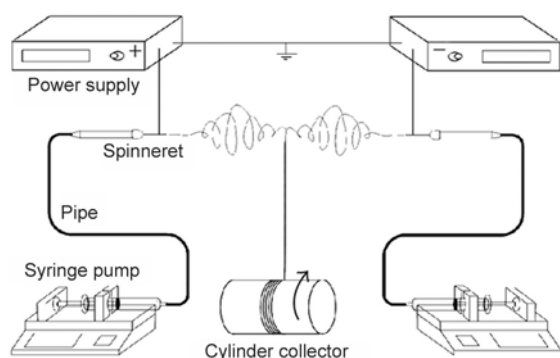


Figure 3. Schematic representation of other side-by-side electrospinning (Reprinted with permission from Xu *et al.* [125] Copyright © 2012 Fu Xu *et al.*)

(9.0% w/v PEGDA) connected by Teflon tubing. A voltage of 18 kV was applied with a TCP of 10 cm. The primary syringe feeding rate was $20 \mu\text{L}\cdot\text{min}^{-1}$ and secondary syringe feeding rate was maintained at $5 \mu\text{L}\cdot\text{min}^{-1}$ to yield a final 3,3'-dithiobis(propanoic dihydrazide)-modified HA (HA-DTPH) concentration of 2.0% (w/v) in the mixture. Ultrafine nanofibres with diameters of $90\pm 15 \text{ nm}$ were obtained. The fibrous structure was maintained after dissolution of PEO in water, but the average diameter moved to $110\pm 28 \text{ nm}$.

The most convenient way to electrospin two polymers is through blending the two or more polymers in a suitable solvent [127]. In this case, the selection of the polymers and the solvent is important due to

the fact that the interactions between the polymers must not cause phase separation during electrospinning. Nonetheless, the proposition to use a single nozzle with two polymer solutions lying in a side-by-side fashion and coming into contact at the tip of the needle and flowing towards the counter electrode overcame the complications of blending the polymers [127]. This technique is known as side-by-side dual spinneret (Figure 4) [128]. These authors synthesized bicomponent nanofibres made up of two small fibres bound together and respectively containing titanium dioxide (TiO_2) and tin dioxide (SnO_2). This was confirmed by SEM-EDS results showing that TiO_2 and SnO_2 were on different surfaces of the fibre.

4.4.2. Co-axial electrospinning

Other designs include co-axial electrospinning where hollow or core-shell fibres can be produced with easy functionalization (Figure 5). Various materials such as polymers, oligomers, nanoparticles, metal salts, proteins, oils, and enzymes immobilized into the core can be produced to achieve integrated multifunctional materials [1, 129–132]. Coaxial electrospinning offers an avenue to prepare nanofibres from the materials which are difficult or impossible to be electrospun into nanofibres using conventional electrospinning processes [129, 132]. It can be used in various applications where the stability and control release of small molecules are of significance [133–136]. With appropriate choice of solvent and components a variety of functionalised hollow structures can be fabricated from blend to composite materials [134]. A core-shell of collagen-r-poly(ϵ -caprolactone) was prepared by this technique [136]. The inner and outer solutions were – poly(ϵ -caprolactone) (PCL)/trifluoroethanol (TFE) ($100 \text{ mg}\cdot\text{mL}^{-1}$) and collagen/TFE ($72 \text{ mg}\cdot\text{mL}^{-1}$), respectively. TEM revealed a core-shell structure with a dark PCL component inside with a diameter $385\pm 82 \text{ nm}$, and a lighter collagen shell with a thickness of $64\pm 26 \text{ nm}$. The variation of the concentration of the solutions for the inner and outer layers influences the overall diameters of the nanofibres, the thickness of the shell and the diameter of the core. Gulfam *et al.* [137] produced porous co-shell structured nanofibres by utilizing a collecting water bath. They varied the concentration of PCL (outer shell) to evaluate its effect on the overall diameter of the resulting nanofibres. The overall diameters of the gelatin-

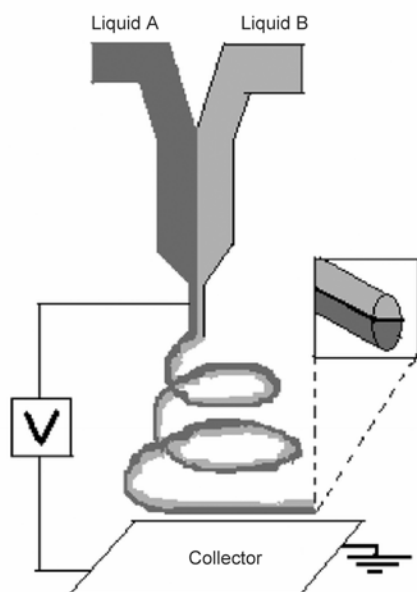


Figure 4. Schematic diagram of side-by-side dual spinneret (Reprinted with the permission from Liu *et al.* [128]. Copyright (2007) American Chemical Society)

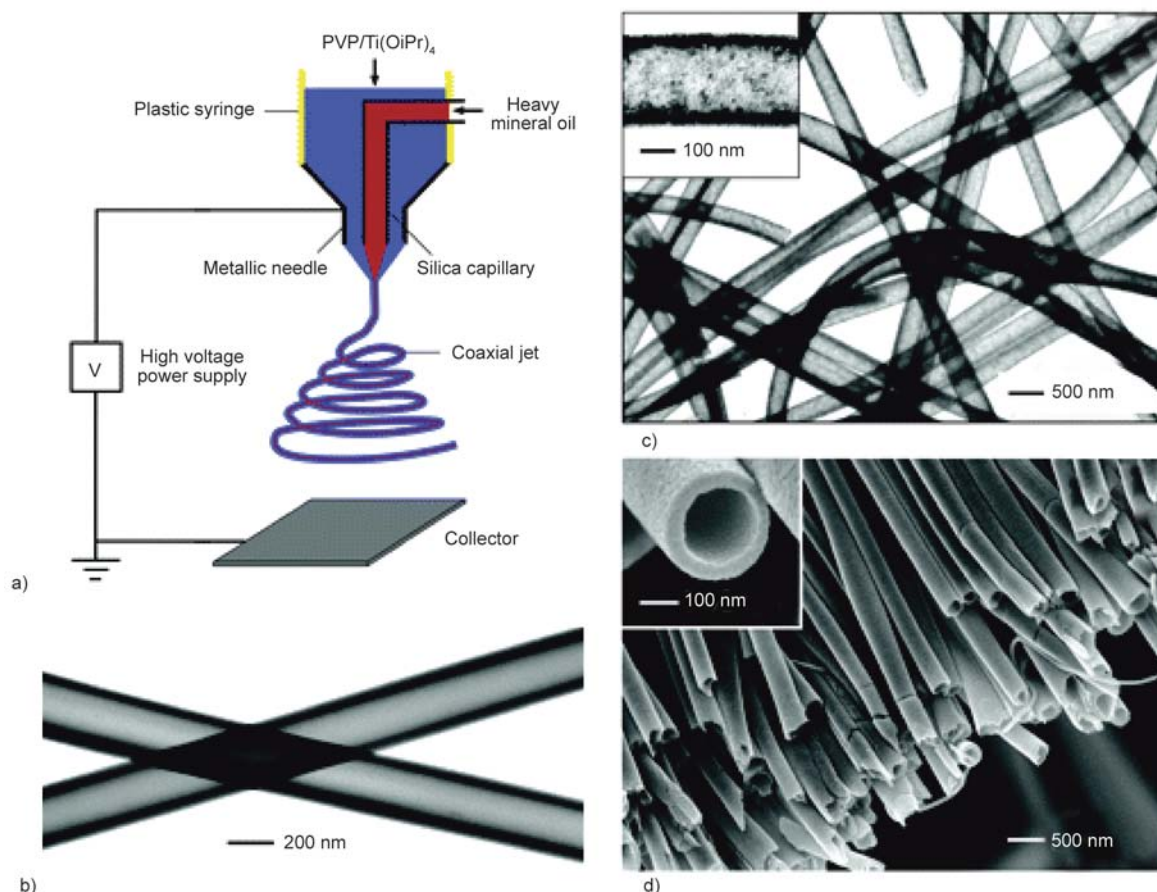


Figure 5. Schematic representations for co-axial electrospinning (a). It consists of a spinneret with two coaxial capillaries in which the polymer solution, mineral oil and functional group are ejected simultaneously to fabricate functionalized hollow fibres. TEM image of two as-spun hollow fibres (b). TEM image of TiO_2 (anatase) hollow fibres (c). SEM image of a uniaxially aligned array of anatase hollow fibres (d). (Reprinted with the permission from Li and Xia [134]. Copyright (2004) American Chemical Society).

PCL core-shell nanofibres gradually increased with an increase in PCL concentration from 105 ± 31 nm at 4% PCL to 210 ± 49 nm at 12% PCL.

4.4.3. Tri-axial electrospinning

Additional to the conventional co-axial electrospinning, various researchers developed a novel tri-axial electrospinning technique [130, 138, 139]. The method uses a nozzle with three concentric needles and three solutions are delivered by different pumps to meet at the tip of the nozzle. Liu *et al.* [140] produced multi-layered biodegradable nanofibres made of gelatin as core and sheath and PCL as middle layer by triaxial electrospinning (Figure 6). The gelatin shell (17 wt%) and core (10 wt%) solutions in 80/20 w/w TFE/deionized water and middle layer PCL (11 wt%) solution in TFE were fed from the triaxial concentric nozzle at 1.0, 0.15, and 0.4 $\text{mL} \cdot \text{h}^{-1}$, respectively. The confocal fluorescence microscopy (with the aid of dyes) and FIB-SEM images con-

firmed the presence of the gelatin/PCL/gelatin layers. The thickness of the sheath was 130 nm, that of the intermediate layer 240 nm, and that of the core layer 230 nm. Even miscible and immiscible polymer solutions, that were impossible to electrospin with traditional co-axial electrospinning, can be fabricated by introduction of the solvent between the two solutions and a reasonable flow rate [130, 140]. The incorporated multilayers can perform different functions and incorporate functional groups to target specific applications of the nanofibres.

5. Electrospinning of biopolymers

A wide array of biopolymers have been electrospun into ultrafine fibres with some difficulty due to the rigid structure and lack of solubility in common solvents. The functional groups, biocompatibility, biodegradability and non-toxicity of biopolymers are unique properties that afford their applications in various fields. The major disadvantage of some bio-

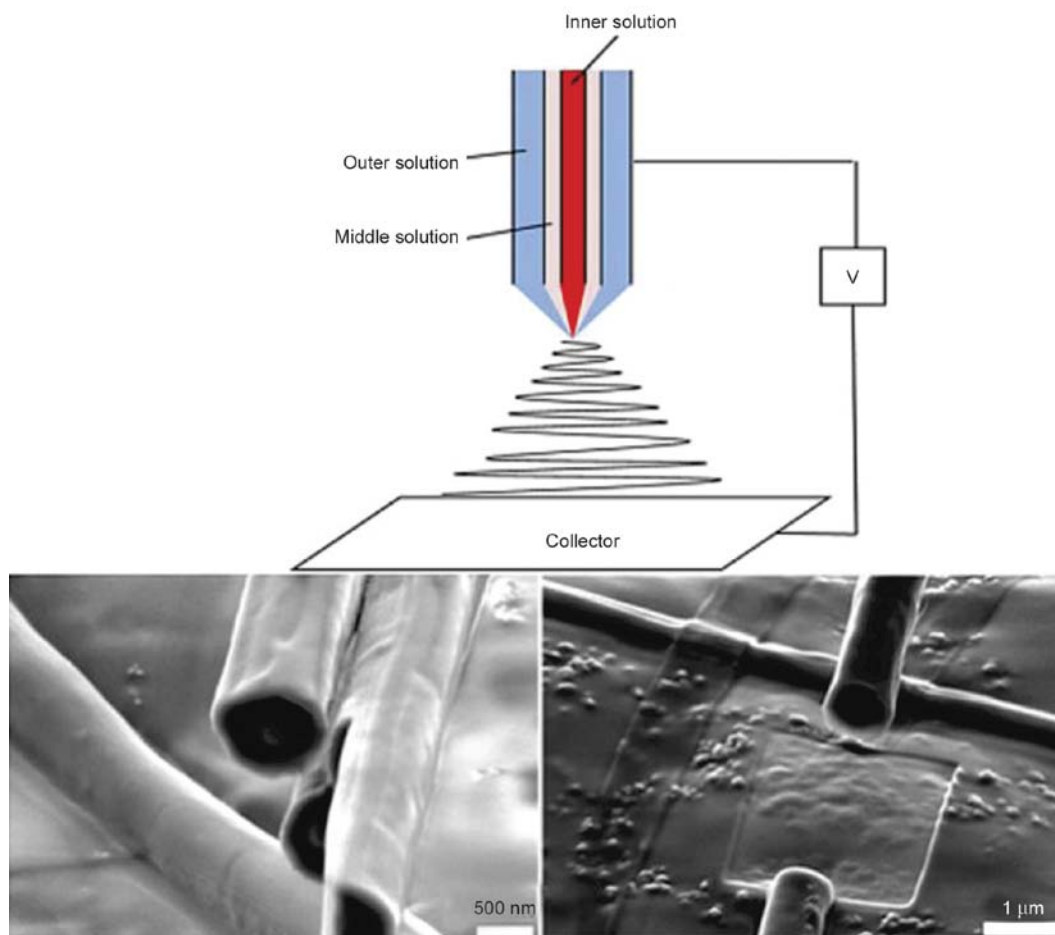


Figure 6. Schematic presentation of triaxial and FIB-FESEM images of triaxial electrospun nanofibres (Reprinted with permission from Liu *et al.* [140]. Copyright (2013) American Chemical Society.)

Table 4. The potential applications of electrospun biopolymer membranes in water treatment

Biopolymer	Desirable properties	Current application	Potential future applications
Cellulose and derivatives	Easy functionalization, hydroxyl groups, and functional groups from derivatives	Drug delivery, food, tissue scaffolds, personal care, detergent, paper making, textile, mining flotation, Pharmaceuticals, personal care, cigarette filters	Bioadsorbent, metal and impurities separation, ultrafiltration, microfiltration and bioadsorbent, trace metal detection
Cellulose nanowhiskers	High specific area, easy functionalization, high crystallinity, high modulus	Polymer reinforcement	Selective layer in ultrafiltration and nanofiltration membranes, microfiltration, reinforcement
Chitin and derivatives	Easy functionalization, availability of amino groups and other functional groups from derivatives	Drug delivery, environmental engineering, tissue scaffolds, food wraps, flocculants in water, biocidal membranes, tissue scaffolds	Anti-biofouling membranes, membrane coating, flocculation agent
Chitin nanowhiskers	High specific area, easy functionalization, high crystallinity, high modulus	Polymer reinforcement	Barrier layer in TNFC, reinforcement
Alginate	Carboxyl groups and hydroxyl groups	Food texturing, tissue scaffolds	Metal chelation, anti-biofouling membrane, heavy metal detectors
Collagen	Unique triple-helical structure	Food, tissue scaffolds, cosmetics	Metal chelation
Gelatin	Thermoreversible viscosity, independent of pH	Cosmetics, food industry, pharmaceutical, coatings	Membrane coating, controlled release and encapsulation of disinfection agents
Hyaluronic and derivatives	Easy functionalization	Dermal fillers, tissue scaffolds	Metal chelation
Aloe vera	Different functional groups	Antibacterial creams, lotions, ointment, tissue scaffolds	Immobilizer of bacteria, enzymes and other biological molecules

polymers in water treatment is their solubility and biodegradation in an aqueous medium, giving the edge to synthetic polymers to be the most applied in water filtration and treatment. As already mentioned earlier, different metal oxides were incorporated into the polymers to enhance their biocidal efficacy and the mechanical strength of the electrospun membranes. Most of these biopolymers bear unique functional groups that can be explored in wastewater treatment to adsorb various heavy metals via different mechanisms such as chelation, electrostatic attraction and ion-exchange. They have abundant availability, biocompatibility, large surface-to-area ratio, high porosity, and malleable mechanical properties and structure, with some unique and interesting potential applications (Table 4).

5.1. Cellulose

Cellulose is the most abundant natural polymer on earth derived from a wide variety of cellulose-containing sources such as plants, animals and bacteria [26, 141]. It is composed of a linear chain of $\beta(1-4)$ linked D-glucose units as shown in Figure 7. Cellulose has interesting properties such as biocompatibility, biodegradability, and recyclability. Electrospinning of pure cellulose, from its aqueous solutions, like most biopolymers poses many challenges, where some modifications of the electrospinning setup/devices are needed [11, 14]. For example, Frenot *et al.* [11] found that the collected fibre stood straight up on the collector when plastic and aluminium covered plates are used as collectors. However, the use of a rotating drum/copper or liquid bath collector in a suitable humidity resulted in smooth bead-free fibres [76, 142, 143]. Cellulose cannot melt and is insoluble in water and most of the common organic solvents because of the dense hydrogen network which limits its applications and processability. Only a few solvents such as paraformaldehyde (PF)/N,N-dimethylformamide (DMF), lithium chloride (LiCl)/N,N-dimethylacetamide (DMAc), N-methylmorpholine-N-oxide (NMMO), urea/sodium

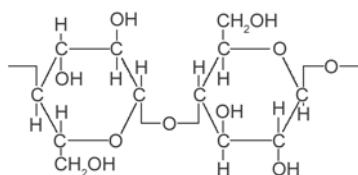


Figure 7. Structure of cellulose

hydroxide (NaOH) and ionic liquids can dissolve cellulose [23, 76].

The possibility to functionalize cellulose *via* the hydroxyl side groups on the backbone offers the opportunity to electrospin it in a derivative-form followed by its regeneration *via* deacetylation or hydrolysis treatments.

The cellulose derivatives through $-OH$ (hydroxyl group) functionalization include cellulose acetate, hydroxyl propyl cellulose, hydroxyl propyl methyl cellulose, and methyl cellulose [11]. These derivatives are soluble in most of the common organic solvents and they can be converted to pure cellulose *via* hydrolysis and deacetylation. Stephen *et al.* [142] functionalized cellulose nanofibrous membrane with oxolane-2,5-dione to enhance their heavy metal adsorption efficiency. They first electrospun cellulose acetate, followed by deacetylation of the resulting nanofibres membrane using sodium hydroxide (0.3M NaOH) to generate pure cellulose. The nanofibrous membrane displayed a large surface area of $13.7 \text{ m}^2 \cdot \text{g}^{-1}$ compared to raw cellulose fibres membrane with a surface area of only $3.2 \text{ m}^2 \cdot \text{g}^{-1}$. The adsorption capacity for lead (Pb) and cadmium (Cd) were respectively 1.0 and $2.9 \text{ mmol} \cdot \text{g}^{-1}$. The regeneration of the mats was done through nitric acid (HNO_3) treatment, and the regenerated mats performed quite well.

5.1.1. Cellulose nanowhiskers

Cellulose nanowhiskers can be extracted from their abundant source (cellulose) by mechanical and chemical means [141, 144]. The high aspect ratio, high crystallinity, easy functionalization, and large surface areas make the nanowhiskers the next generation of wastewater treatment nanomaterials. Several researchers incorporated various whiskers in different polymers such as poly(2-hydroxy ethyl methacrylate) [145], PVA [146], and PEO [147] to improve the mechanical properties of the resulting electrospun nanofibres. These researchers found that the higher modulus and stiffer nanowhiskers improved the mechanical properties of the electrospun nanofibres despite the observed agglomeration of the whiskers [147].

Oxidized jute cellulose whiskers with diameters ranging between 3 and 10 nm were coated onto polyacrylonitrile (PAN) nanofibres membrane (mean diameter $\sim 173 \text{ nm}$) either once (single layer) or

twice (double layer) by using a glass rod [148]. This method afforded pore sizes ranging between 5 and 65 nm. The membrane was tested under both ultrafiltration (UF) and nanofiltration (NF) conditions, in which the rejection of both nanosilica (in the case of UF) and oil and water (in the case of NF) was above 99%. The mechanical properties of the resulting electrospun nanofibrous membrane (ENM) were improved by the presence of the whiskers, with the tensile strength increasing from 4 to 10 MPa (for one coating of the whiskers onto the ENM) and 14 MPa (for double coating).

Cellulose nanowhiskers and nanofibres have also been thoroughly studied by the Chu and Hsiao group in water treatment and filtration applications [149–152]. The cellulose nanowhiskers were either employed as barrier layer of thin-film nanofibrous composite membranes (TFNC) (Figure 8), or they were infused into the electrospun membrane, depending on the intended filtration application (microfiltration (MF) or UF).

The cellulose nanowhiskers were prepared through a [2.2.6.6-tetramethylpiperidinoxy (TEMPO)/sodium bromide (NaBr)/sodium hypochlorite (NaClO)] oxidation method. The length of the cellulose nanowhiskers ranged between 200 and 400 nm and the diameters between 5 and 10 nm. In the case of MF, the infusion of the whiskers resulted in a reduction of the mean pore size with a narrower dis-

tribution than the electrospun PAN nanofibrous membrane. In comparison with the commercial membrane GS0.22 made of nitrocellulose and acetyl cellulose ester, the water flux cellulose nanowhiskers-based membrane was better because of the difference in porosity (>80% versus 52%) [144]. The mechanical properties were improved with Young's modulus and tensile strength values of 375 ± 15 and 14.3 ± 0.4 MPa, respectively, compared to the unmodified membrane (226 ± 20 and 8.5 ± 0.3 MPa) which was still higher than the commercial membrane with a tensile strength of 5.6 ± 0.3 MPa. The adsorption of crystal violet (CV) dye was better in the case of the cellulose nanowhiskers-based membrane than in GS0.22 (Figure 9a). The adsorption was two times higher at $10 \text{ mg} \cdot \text{L}^{-1}$ of CV dye with a high rate of adsorption because of the hydrophilicity and large surface area. The adsorption data fitted the Langmuir isotherm showing monolayer adsorption (Figure 9b). The adsorption capacity was 16 times higher for the cellulose nanowhiskers-based membrane. The cellulose nanowhiskers as a thin barrier layer in TNFC displayed superior performance compared to the commercial known membranes [144]. The hydrophilicity, large surface area to volume ratio and the surface charges of the cellulose nanowhiskers played a significant role in improving the rejection and flux of the membrane.

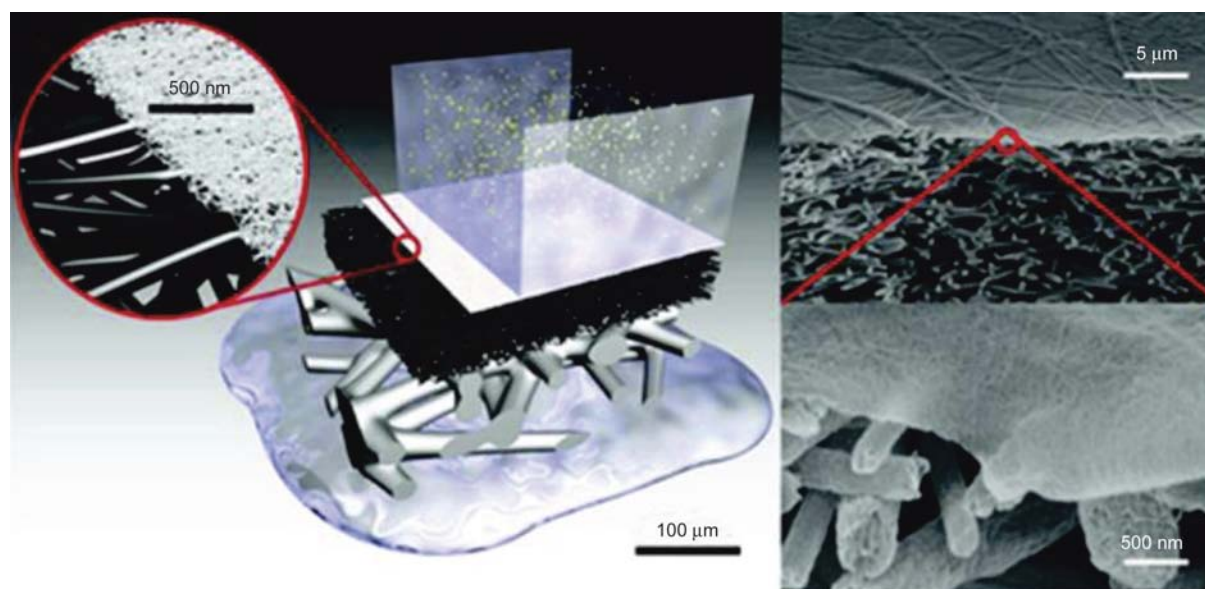


Figure 8. (Left) A schematic representation of a thin-film nanofibre composite membrane (TNFC) with three layers: selective/barrier layer, mid-layer of electrospun nanofibres, and nonwoven supporting mat (poly(ethylene terephthalate) (PET)). (Right) Cross-sectional SEM views of the barrier layer and electrospun nanofibres in a typical TNFC membrane. (Reprinted with permission from Ma *et al.* [150]. Copyright (2012) American Chemical Society).

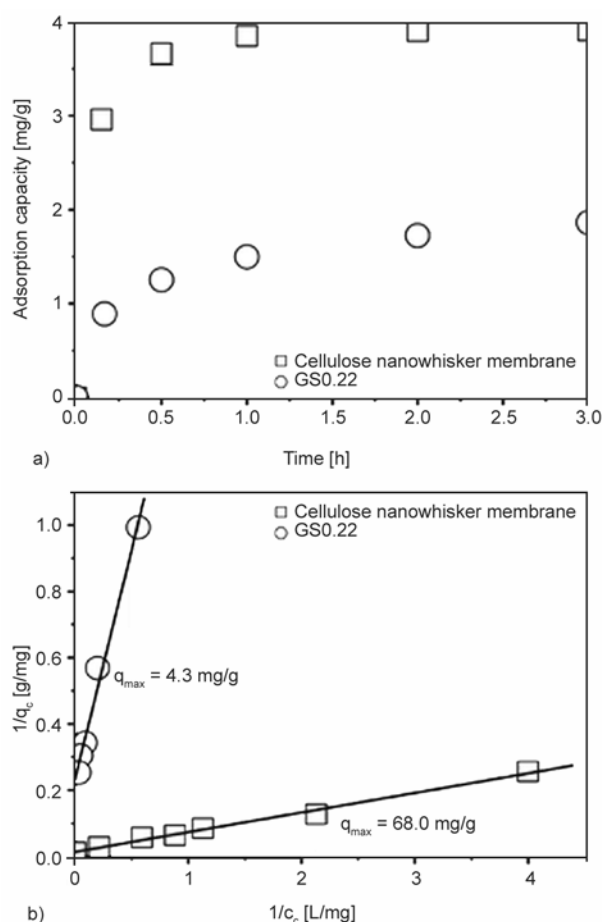


Figure 9. (a) Adsorption capacity of cellulose nanowhiskers-based nanofibrous MF membrane and GS0.22 against time; (b) respective Langmuir adsorption isotherms for the two membranes (Reprinted with permission from Ma *et al.* [144]. Copyright (2012) American Society.)

5.1.2. Cellulose derivatives

Cellulose acetate

Among the cellulose derivatives, cellulose acetate (CA) is the most studied derivative due to its potential to regenerate pure cellulose via deacetylation [23, 152]. Cellulose acetate is synthesized by acetylation of the hydroxyl groups on cellulose with an average of 2–4 degree of substitution per glucose units (Figure 10). The CA enjoyed its success in membrane filtration for more than seven decades

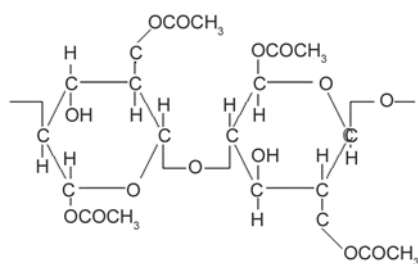


Figure 10. Structure of cellulose acetate

now [149, 153, 154]. It has been widely used as a selective layer in nanofiltration and ultrafiltration. With its unique functional groups that can be modified, it is rated as one of the good metal adsorbents [149, 150]. The functionalization of CA with –COOH, –SO₃H and NH₂ offers an opportunity for the application of CA in heavy metal complexation [155–158]. Some nanofillers can be added to a cellulose acetate membrane to enhance the metal adsorption capacity [149, 155, 156].

Zhou *et al.* [159] prepared cellulose acetate nanofibrous membranes from various solvents (dichloromethane, formic acid, acetic acid, and trifluoroacetic acid). Only trifluoroacetic acid afforded the production of smooth nanofibres with diameters ranging between 100 and 300 nm. This membrane displayed a porosity and surface area of respectively 87% and $2.02 \cdot 10^7 \text{ m}^{-1}$ with high water permeability and hydrolytic stability. Aluigi *et al.* [61] studied the influence of various solvents and their mixtures on the electrospinning of CA. Using a single solvent like chloroform, N,N-dimethylformamide (DMF), dichloromethane (DCM), methanol (MeOH), formic acid, or pyridine, it was not possible to fabricate smooth nanofibres. Only discrete beads were formed, and acetone produced short beaded nanofibres. CA (5% w/v) in a mixture of chloroform-MeOH and DCM-MeOH produced beaded and smooth fibres, especially at 4:1 (v/v). The average diameters were 0.79–1.09 μm and 0.67–1.06 μm respectively for the binary mixtures of chloroform-MeOH and DCM-MeOH. Smooth fibres were formed at solvent mixture concentrations of a 16% (w/v) solution of CA in 1:1, 2:1 and 3:1 acetone-N,N-dimethylacetamide (DMAc), 14–20 % (w/v) solution of CA in 2:1 acetone-DMAc, and 8–12 % (w/v) solutions of CA in 4:1 (v/v) DCM-MeOH. The diameters ranged between 0.14–0.37 μm and 0.48–1.58 μm for fibres prepared from acetone-DMAc and DCM-MeOH, respectively.

Chen *et al.* [160] functionalized cellulose acetate nanofibrous membrane with chlorhexidine for their biocidal efficacy. To facilitate electrospinnability in N,N-dimethylformamide (DMF), high molecular weight PEO was added. The electrospun nanofibrous membrane was crosslinked using titanium triethanolamine in isopropanol. The biocidal efficiency against *E. coli* and *S. epidermidis* increased with concentration of chlorhexidine. The membrane displayed biocidal efficiency above 99%. Moreover,

different drugs can be incorporated in cellulose acetate as carrier [69, 161, 162]. Suwatong *et al.* [162] incorporated curcumin in cellulose acetate nanofibres to investigate its releasing character. The cellulose acetate nanofibres retained their structure and morphology after the addition curcumin. A 95% release without toxicity was established. This property can be explored in incorporating different functions/biocides for controlled release in water treatment. For example, Ma and Ramakrishna [163], covalently bond protein A/G onto the oxidized CA membrane to bind IgG molecules and a capturing capacity of 18 $\mu\text{g}/\text{mg}$ was reported. Similarly, Chen *et al.* [164] functionalized hydrolysed CA with cobalt tetraaminophthalocyanine (CoPc) for the adsorption of reactive red X-3B dye and more than 95% of the dye was eliminated within 3 hours.

Other cellulose derivatives

Four different carboxymethyl cellulose sodium salts (CMC) were electrospun by Frenot *et al.* [11]. CMCs with different molecular weight and degree of substitution were electrospun in the presence of PEO as copolymer, dissolved in a water and ethanol mixture at a ratio of 1:1. The nanofibres displayed similar homogeneous structures with mean diameters of 200–250 nm, regardless of the molecular weight and degree of substitution. In the same study, two hydroxypropyl methyl cellulose (HMPC) samples with equal M_w , and with varying contents of methoxy and hydroxypropoxy groups, were compared. Mean diameters of 127 and 128 nm were obtained for the two HMPCs, regardless of the functional group contents, but at different spinnable concentrations. Lim *et al.* [88] studied the effect of different parameters (concentration, voltage, flow rate and tip-to-collector distance) on the electrospinning of ethyl cellulose (EC). At a low concentration (6 wt%) a mixture of smooth and beaded-fibre structures was observed, which disappeared as the concentration was increased to 8 wt% of the EC and above. The mean diameter of the nanofibres gradually increased with flow rate, whereas an increase in voltage reduced the mean diameter of the nanofibres.

5.2. Chitin

Chitin is the second most abundant natural polymer on earth after cellulose. It appears as ordered crystalline structure of microfibrils in the exoskeleton of arthropods, and the cell walls of fungi and yeast

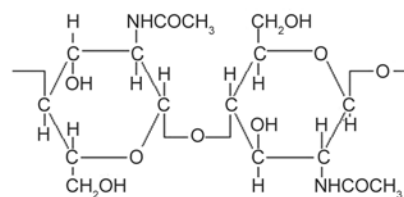


Figure 11. Structure of chitin

[165]. Chitin, the mucopolysaccharides that is made up of β -(1-4)-N-acetyl-D-glucosamine units linked by 1-4 glycosidic bonds, acts as mechanical strength and supporting structure in crustaceans, insects, etc. (Figure 11) [51, 166, 167]. Chitin with desirable properties such as good biocompatibility, biodegradability and ubiquitous availability has been used in various fields such as cosmetic, biomedical and in food additives [165].

Very few studies dealt with electrospinning chitin from its aqueous solution, because of its poor solubility [168, 169]. In these studies the solubility of chitin was enhanced by Co^{60} gamma ray irradiation. Chitin nanofibres with diameters ranging between 50 nm and several microns were electrospun in 1.1.1.3.3.3-hexafluoro-2-propanol (HFIP), with the diameters depending on the electrospinning technique parameters such as concentration [167–169]. Min *et al.* [168] irradiated chitin (200 kGy) and obtain an average molecular weight of 91 000 to enhance its dissolution in HFIP. They produced chitin nanofibres with a broad fiber diameter distribution (40 to 640 nm) and most were less than 100 nm.

5.2.1. Chitin nanowhiskers

The nanocomposites of PVA and chitin whiskers were reported for the first time by Junkasem *et al.* [170]. Nanowhiskers with the lengths in the range 231–969 nm and widths of 12 to 65 nm were produced. Nanocomposite nanofibres (prepared from water) with diameters ranging between 175 and 214 nm, depending on the concentration of the chitin whiskers, were obtained. The thermomechanical properties of PVA were enhanced by the presence of the chitin whiskers [171]. Naseri *et al.* [172] reinforced a blend of chitosan and PEO with chitin nanowhiskers. The modulus and tensile strength were significantly increased from 0.4 to 4.3 GPa and from 4.6 to 34.9 MPa, respectively. An antibacterial TNFC membrane was developed by including chitin nanowhiskers as barrier layer onto electrospun PAN nanofibres (as a mid-layer on top of a PET nonwoven support) [144]. The flux permeation was

217.0 L·m⁻²·h⁻¹ (which was 8–10 times higher than that of commercial PAN10) for two days at 30 psi with a rejection above 99.7%.

5.2.2. Chitin with synthetic/biopolymers

A nanofibre blend of poly(glycolic acid) (PGA) and chitin was prepared by Park *et al.* [173]. The nanofibres had a broad diameter distribution in the range of 50–350 nm, with most of the nanofibres having an average diameter of 150 nm. Chitin/silk blend nanofibres were prepared by several researchers using HFIP as a solvent [124, 173]. The nanofibres had diameters ranging between 340 to 920 nm depending on the content of silk in the composite material. Irradiation and little deacetylation (8% DD) of chitin was also adopted to reduce its molecular weight and improve its solubility.

5.2.3. Chitin derivatives

Dibutyl chitin

One of the readily soluble chitin derivatives in most common organic solvents (acetone, ethanol) is dibutyl chitin. It is synthesized from butyric anhydride and perchloric acid. Błasiński *et al.* [174] electrospun an ester derivative of chitosan, dibutylchitin (DBC), from ethanol. 9 wt/v of DBC at 25 kV was the optimal conditions to establish bead-free nanofibres with a transverse dimension of 0.3 µm. DBC and a cellulose acetate hybrid were electrospun in a 1:1 ratio of acetone and acetic acid [175]. The mixture of CA/DBC at a concentration of 5% from 100/0 to 0/100 ratio compositions produced bead-free nanofibres with 30–350 nm diameters. Pant *et al.* [176] synthesized chitin butyrate from a mixture of butyric acid, trifluoro acetic anhydride and phosphoric acid, followed by the addition of ethyl alcohol and filtration. The resulting solution was washed repeatedly with diethyl ether and water, followed by drying for 3 days in a hood and then in a 60°C oven for 6 hours. The resulting butyric chitosan was electrospun with nylon-6 in formic acid/acetic acid to give spider-web-like nanofibres with an average diameter of 15 nm at a low butyric chitosan content (90/10 nylon-6/butyric chitosan).

Carboxymethyl chitin

To circumvent the solubility issues of chitin and chitosan, some of their derivatives have been electrospun into nanofibres either from their aqueous solutions or by blending with other polymers. This

not only improved their spinnability, but also alleviated the use of a toxic solvent utilized in electrospinning both chitin and chitosan. Carbomethyl chitin (CMC) is one of the chitin derivatives that are readily soluble in water. However, the electrospinning of CMC from its aqueous solution results in spherical drops [177]. Nevertheless, ultrafine nanofibres from a CMC/PVA blend at a 20:80 ratio (CMC (7%):PVA (8%)) was reported. Sohofi *et al.* [178] were the first to fabricate CMC electrospun nanofibres from its aqueous solutions using binary solvents. The 6 wt% CMC (with degree of substitution of 0.65) was electrospun in a 30/70 dichloromethane/trifluoroacetic acid mixture to ultrafine nanofibres with an average diameter of 260±42 nm. Although the carbomethylated chitosan showed a potential in metal adsorption [179], nanofiltration [180], and microfiltration [181] processes, not much has been done on electrospun CMC in wastewater treatment.

Chitosan

Chitosan results from the deacetylation of chitin under alkaline conditions, or from enzymatic hydrolysis in the presence of chitin deacetylase. It is an aminopolysacchride with unique properties and functionalities for a wide spectrum of applications from biomedical to industrial areas. Chitosan is a copolymer made up of 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-glycopyranose linked together through (1-4)-β-glycosidic bonds (Figure 12). Similar to alginates, different forms of chitin and chitosan such as gels, membranes, beads, microparticles, nanoparticles and nanofibres have been produced for various applications [51, 166]. Chitosan is well-known for its unique antimicrobial activity and metal adsorption [182, 183]. These result from the protonation of NH₂⁺ groups on its backbone. It is capable of chelating ions from aqueous media and inhibiting the growth of a broad spectrum of fungi, yeasts and bacteria. The cations along the chitosan repeating units can be varied through deacetylation. A higher the degree of deacetylation results in a larger number of cations on the backbone of the chi-

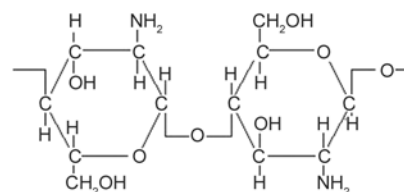


Figure 12. Structure of chitosan

tosan. Chitosan is soluble in most acids, which protonate it into a polyelectrolyte.

Different solvents such as dilute hydrochloric acid, acetic acid, formic acid and trifluoroacetic acid (TFA) were tested to envisage the electrospinnability of chitosan [184]. Only with TFA as solvent chitosan nanofibres were successfully established [184]. It was indicated that the TFA either forms amino groups on chitosan, which results in the destruction of the rigid interaction between the chitosan molecules, or that the high volatility of TFA caused rapid solidification of the electrified jet. More homogeneous nanofibres were obtained by addition of dichloromethane, due to its high volatility. Geng *et al.* [67] successfully electrospun chitosan from concentrated acetic acid. 30% of acetic acid in water resulted in a combination of droplets and thinner nanofibres with an average diameter of 40 nm, whereas at 90% acid concentration the diameter of the nanofibres increased to 130 nm without beads.

Chitosan with synthetic polymers

Over the past decades, electrospun chitosan hybrids have been fabricated using various synthetic polymers such as polyvinyl alcohol (PVA) [126, 185], poly(lactide-co-glycolide) (PLGA) [126], polyethylene oxide (PEO) [186], polyvinyl pyrrolidone (PVP) [83], poly(lactic acid) (PLA) [80], and poly(ethylene terephthalate) (PET) [187]. Interestingly, the synthetic polymer did not only improve the electrospinnability of chitosan, but significantly enhanced the biocompatibility, antibacterial, mechanical strength and other properties of the hybrid nanofibres. These broadened the applicability of the chitosan-based nanofibres in a broad spectrum of applications. PEO is a biocompatible synthetic polymer favourable for biomedical and tissue engineering. Su *et al.* [186] prepared chitosan/PEO blends doped with monovalent (Na^+), divalent (Ca^{2+}) and trivalent (Fe^{3+}) metal chlorides to enhance the homogeneity of the resulting nanofibres. They found that these metal chlorides promoted the fibrous morphology of the chitosan/PEO blends, opening doors for the use of these nanofibres in various applications such as wound dressing, bone regeneration, etc.

Chitosan with other biopolymers

The electrospun nanofibres of chitosan and other natural polymer blends were studied by several researchers [188, 189]. Torres-Giner *et al.* [188] pre-

pared a bioblend of chitosan and zein for biocidal applications. Low zein content (1 wt%) in the bioblend resulted in ribbon-like nanofibres with an average diameter of 320.9 ± 92.3 nm. An increase in the percentage of chitosan in the blend yielded beaded-fibres with smaller average diameters between 161.7 ± 39.6 and 128.5 ± 26.2 nm. The electrospun bioblend inhibited bacterial growth. Bioblend electrospun nanofibrous membrane of chitosan and a type I collagen were fabricated with the aid of PEO, followed by crosslinking with glutaraldehyde [190]. The ultrafine fibres had average diameters of 134 ± 42 nm before crosslinking and 98 ± 76 nm after crosslinking. The difficulty of electrospinning CS/collagen, due to its high conductivity/charge density, was improved by the addition of PEO. Young modulus was improved from 0.29 ± 0.04 to 0.65 ± 0.02 MPa by crosslinking. Maeda *et al.* [191] electrospun chitosan with the aid of PEO, followed by coating with hyaluronic acid. The composite was made by dissolving PEO in water and coating with hyaluronic acid, and it was stable in water with an improved swelling ratio due to the increased hydrophilicity as a result of the presence of hyaluronic acid. PVA/CS was electrospun onto a PVDF micro-filter, followed by crosslinking with glutaraldehyde [192]. The membrane was immersed in glutaraldehyde (5 mM) and an HCl (0.01 N) solution for six hours, and the membrane shrunk by ~5%. Dead-end filtration was utilized to evaluate the metal adsorption capacity of the membrane. A 5% adsorption capacity was reported.

Chitosan derivatives

Quaternized chitosan (QCh) nanofibrous membrane for antibacterial activity were electrospun by Ignatova *et al.* [83, 193, 194] using poly(vinyl pyrrolidone), polyvinyl alcohol, and poly(lactic acid). The addition of these synthetic polymers significantly improved the electrospinnability of quaternized chitosan. The composite nonwoven mats showed good antibacterial activity against Gram negative and Gram positive bacteria. Kangwansupamonkon *et al.* [195] prepared chitosan/PEO mats followed by functionalization to form N-(2-hydroxyl) propyl-3-trimethyl ammonium chitosan chloride (HTACC) and N-benzyl-N,N-dimethyl chitosan iodide (QBzCS) membranes. They prepared the nanofibres from a blend of chitosan and PEO (6.7:0.3% w/v) in a mixture of trifluoroacetic acid/dichloromethane (70/30 v/v) followed by functionalization. They obtained

ultrafine nanofibres with average diameters of 272 ± 56 nm. The membranes displayed good antibacterial efficiency against both *S. aureus* and *E. coli*. Ultrathin nanofibres of N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (HTTC) through blending with PVA was reported by Alipour *et al.* [196]. The HTTC was synthesized from a reaction between chitosan and glycidyl-trimethylammonium chloride. The water soluble derivative, HTTC, was electrospun through blending with PVA to give nanofibres with 200–600 nm diameters. Good antibacterial efficiency was reported for these membranes.

Chitosan can be modified by various acyl chlorides (dodecyl, hexanoyl, decanoyl, and lauronyl) in the presence of mixed pyridine and chloroform as solvents [197]. These modifications are usually adapted to improve the solubility of the chitosan. Hexanoyl-chitosan from chitosan modification by hexanoyl chloride in chloroform was electrospun by Neemark *et al.* [82]. The ribbon-like fibres with average diameter of 3.93 ± 1.82 μm at a concentration of 14% w/v were obtained. This was due to the rapid evaporation of the chloroform from the electrified jet. Peesan *et al.* [198] fabricated a blend of hexanoyl chitosan/polylactide using chloroform, dichloromethane and tetrahydrofuran as solvents. The smooth bead-free nanofibres were obtained at 50 wt% of chitosan in the blends using chloroform as spinning solvent. Patanaik *et al.* [27] electrospun lactic acid modified chitosan using TFA as solvent and MC as co-solvent. The nanofibres were stabilized using thermal treatment to convert the lactate to lactamide. The resulting nanofibres showed good nanofibrous integrity, even after exposure to a BSA medium for 72 hours.

Different molecular weights (40–405 kDa) and degrees of substitution (DS) (0.25–1.19) carbomethyl chitosan (CMCS) were synthesized via chitosan alkylation, followed by carbomethylation with monochloroacetic acid [81]. Despite the difference in DS and M_w , and with the incorporation of Triton X-100 (to reduce both solution surface tension and conductivity) into the aqueous CMCS solution, the spinning solution still led to drops (6–20% concentration). The blending of the CMCS with hydrosoluble synthetic polymers (PVA, polyacrylic acid (PAA), polyacrylamide (PAAm) and PEO) enhanced the spinnability of CMCS into smooth nanofibres, but it depended on the polymer used. PEO (100 kDa) with

30% CMCS gave merged non-cylindrical nanofibres mostly with 300 nm diameter, while PAAm at 1/10 w/w of 5000 kDa/10 kDa (18 wt%) resulted into a similar structure as the PEO/CMCS blend. A 10 wt% binary aqueous mixture with equal mass PAA (450 kDa), produced straight cylindrical nanofibres with elongated beads (100 nm diameter). A mixture of PAAm and PAA resulted in higher CMCS content (50%), but with a large number of beads. In the case of a PVA binary solution with a concentration of 8.5 wt% (CMCS 405 kDa), nanofibres with average diameters ranging between 210 and 170 nm were obtained on increasing the CMCS content from 20 to 50%. The PVA/CMCS system is therefore feasible to produce bead-free nanofibres. The stability of the PVA/CMCS in water was further enhanced by heat treatment at 140°C for 30 minutes.

Another interesting approach to overcome the problem of solubility of chitosan is PEGylation. Du and Hsieh [84] synthesized PEG-N-chitosan and PEG-N,O-chitosan *via* reductive amination and acylation of the chitosan. A small DS value of 0.2 for the solubility of the derivatives in water was reported. For PEG-N,O-chitosan a DS of 1.5 was sufficient for its solubility in CHCl_3 , DMF, DMSO and THF. Regardless of the degree of substitution of PEG (DS) and the derivative of chitosan, only droplets were collected due to a lack of chain entanglements. All the aqueous solutions of PEG-N-chitosan (from reductive amination) resulted in spraying (drops), regardless of the DS of PEG. Smooth nanofibres with diameters ranging between 40 and 306 nm (average 162) were obtained by increasing the concentration of the PEG-N,O-chitosan with the aid of a surfactant (0.5% Triton X-100™) and co-solvent (75/25 v/v THF/DMF).

5.3. Alginate

Alginate is a well-known polyelectrolyte binary copolymer derived from seaweeds/algae [199–202]. It contributes to the flexibility and strength of the seaweeds against adverse water forces. It is usually found in the cell wall matrix and intercellular material (mucilage). Alginate is a linear polysaccharide made up of D-mannuronic (M) and L-guluronic (G) units linked together by 1–4 glycosidic bond (Figure 13). These units appear in varying sequences and ratios, M/G, along the polymer chain depending on the source or specie, the growth conditions, season and depth at which is extracted. The varia-

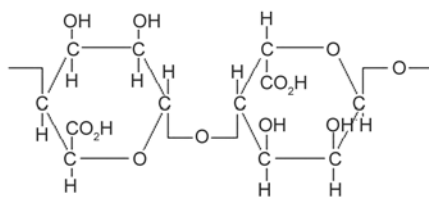


Figure 13. Structure of alginate

tion of M and G along the alginate chain determines its physical properties and reactivity. The molecular conformation and functional groups (especially carbonate ions) have been found to play a significant role in the heavy metal affinity of the alginates [202]. Alginate can gel at room temperature in the presence of polyvalent or divalent metal ions. This phenomenon has been exploited to prepare different morphologies and structures for certain applications. Beads [203], films [204, 205], hydrogels [206], as well as porous membranes and nanofibers [200] were fabricated for different applications such as wound dressings and metal adsorption. There has been significant interest in the use of alginate in biomedical applications because of its antimicrobial efficiency and structural resemblance to glycosaminoglycan (GAG) (one of the significant components of natural extracellular matrices (EMCs) found in mammalian tissues). Furthermore, the good cellular compatibility, non-toxicity, biodegradability, and availability of alginate opened doors for its exploitation in various applications such as metals recovery [202, 203].

Until now the electrospinnability (in this case electrospinnability is used to describe bead-free smooth nanofibres) of sodium alginate is still impossible. In most studies carrier polymers are generally used to improve this. Alginate is readily soluble in water. However, it is still controversial on why it is not possible to electrospin alginate on its own. It has been postulated that a high conductivity, lack of entanglements, and gelation of the alginate solution at low concentration (below the concentration for the formation of entanglements) are responsible for this. The rigidity of the chains, worm-like molecular structure and high surface tension also contribute to this. Nevertheless, Nie *et al.* [12] managed to prepare pure alginate nanofibres using glycol as a solvent. They found that the glycol altered the chain conformation of the alginate and improved chain entanglements (viscosity and elasticity). Glycol decreased the surface tension and conductivity which contributed to the electrospinnability of pure alginate. Bonino *et al.*

[207] tried to electrospin pure alginate using water as a solvent, which resulted in large droplets on the collector, that were reduced by a surfactant. The production of alginate nanofibres from its aqueous solution was also reported by Fang *et al.* [24]. Calcium ions improved the intermolecular interaction which enhanced its electrospinnability from water. 1 wt% Ca^{2+} was sufficient to ensure continuous electrospinning and long nanofibres. The hydrolysis degradation of alginate in water *via* glycosidic hydrolysis after 15 days (reducing alginate solution viscosity) was exploited to electrospin alginate solution (4wt%) with the aid of a Triton X-100 surfactant and dimethyl formamide (DMF) as a cosolvent [208].

5.3.1. Alginate with synthetic polymers

One of the convenient ways to enhance the electrospinnability of biopolymers consists of choosing a compatible copolymer to co-spin with. Polyethylene (PEO) is a biocompatible and biodegradable synthetic polymer. It is non-ionic and hydrosoluble. Alginate is also hydrosoluble and therefore offers the opportunity to co-spin the two without difficulties [54]. The two interact with each other through hydrogen bonding which reduces the viscosity of the alginate solution. Cylindrical nanofibres from alginate/PEO with a mean diameter of ~ 75 nm were prepared by Jeong *et al.* [52]. Recently, Saquing *et al.* [54] reported that higher molecular weight PEO is required to increase the concentration of alginate in the PEO/alginate blend. They indicated that the PEO-PEO interaction is responsible for the electrospinnability of alginate. Co-axial electrospinning of alginate (core) and PEO (shell) was recently reported. PEO was easily extracted by dissolving the nanofibres in water containing calcium chloride to cross-link the alginate [129]. They successfully incorporated 85 wt% of alginate in the blend with the aid of the surfactant. Another hydrosoluble synthetic polymer, with good mechanical properties, thermal stability, chemical stability and biocompatibility, is poly(vinyl alcohol) (PVA). A number of researchers utilized this polymer as copolymer for alginate electrospinning [208–210]. Similar to PEO, the flexible PVA interacts with the alginate *via* hydrogen bonding, thus improving the electrospinnability of the rigid alginate [208]. Different morphologies of PVA/alginate were reported by Lee *et al.* [210]. At low alginate concentrations, ultrafine nanofibres were produced, and when the concentration was increased,

electrospinning led to bigger beads with smaller average distances between the beads.

The solubility of alginate has been one difficulty facing its applicability in various fields. In order to improve the stability of the electrospun alginate, various crosslinking agents were investigated [211]. The electrospun nanofibrous membrane retained their fibrous structure after incubation for 7 days in aqueous medium (BSF). The morphology of the electrospun alginate/PEO blend as vitamin carrier was directly dependent on the viscosity of the alginate [212]. Higher viscosity alginate favoured beaded nanofibres with smaller average diameters, compared to low viscosity alginate-based nanofibres that were bead-free with larger diameters. The most significant part of using PEO as copolymer, beside the fact of enhancing the electrospinnability, is the opportunity to extract PEO from the nanofibres by incubation in water [53]. In this case the alginate is crosslinked through ionic bonds followed by leaching the PEO. A natural surfactant such as lecithin has been used to impart uniformity to the nanofibres [213]. The surfactant readily renders the opportunity to increase the alginate content in the blend without losing the uniformity of the nanofibres.

5.3.2. Alginate with other biopolymers

A blend of gelatin/sodium alginate produced smooth nanofibres in heated water (45°C) [22]. A blend of chitosan and alginate was also electrospun with the aid of PEO as copolymer [214]. Because chitosan is a cationic copolymer and alginate is an anionic copolymer, they form a polyionic complex that does not need further crosslinking. Due to the gelation of these polymers, side-by-side electrospinning was used where the alginate and chitosan meet at the tip of the spinneret. The swelling of the nanofibres was reduced by the incorporation of chitosan which is not soluble in water. Core-sheath morphology of alginate and chitosan was achieved by spinning the alginate into a chitosan coagulation bath [133]. The average diameter of the nanofibres ranged between 600 and 900 nm coated with chitosan. This enhanced the stability of the alginate in saline solution.

5.4. Collagen

One of the most abundant proteins is collagen. Collagen is a kind of protein that gives strength, elasticity and structural support. The two most electrospun collagen types are collagen type I and type III [75,

215]. Collagen is soluble in a water/ethanol mixture, HIFP [216], TFE [217] and acetic acid [218]. Most research based on collagen was aimed to develop collagen nanofibrous membrane from non-toxic solvents, since collagen is usually used in biomedical applications [219]. These authors established that collagen nanofibrous membrane electrospun from fluoroalcohols lost their natural inherited properties. Matthews *et al.* [75] fabricated aligned collagen nanofibres using 1,1,1,3,3,3 hexafluoro-2-propanol as solvent with a rotating drum collector. The nanofibres were randomly oriented at a mandrel rotating speed of less than 500 rpm, and an increase to 4500 rpm aligned the fibres along the rotation axis. Optimization of the collagen nanofibres was studied by Li *et al.* [218]. Through manipulation of the processing and solution parameters it was possible to produce smooth nanofibres with diameters below 100 nm, but at the expense of the fibre structure. A decrease in concentration from 5% gradually reduced the fibre diameter from ~500 to ~200 nm, and a further decrease in concentration led to fibres with diameters below 100 nm, but with significant formation of beads. It was concluded that the minimal concentration of collagen in 1,1,1,3,3,3 hexafluoro-2-propanol to produce smooth and uniform nanofibres is 5%.

5.4.1. Collagen with synthetic polymers

Another feasible approach to avoid the use of toxic solvents is to co-spin collagen with a spinnable polymer. Chakrapani *et al.* [220] produced collagen nanofibrous membrane from a blend of PCL and collagen in acetic acid. The nanofabric network was made up of fibres with diameters ranging between 100 and 200 nm having a porosity of about 60%. Dong *et al.* [20] prepared collagen nanofibres from phosphate-buffered saline (PBS) and ethanol in the presence of the salt (NaCl). They found out that 16 wt% of collagen was readily soluble when the salt was 5 wt% or more. Nanofibres with diameter ranging between 210 and 540 nm, depending on the salt concentration, were produced. A co-axial morphology of collagen (outer shell) and PCL (inner core) as structural support was produced using both TFE and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). The co-axial structure was fabricated by using a co-axial nozzle or by coating the electrospun membrane by immersion into a collagen solution [217]. The co-axially electrospun nanofibres displayed a similar morphology as pure PCL nanofibres, with an aver-

age diameter of 385 ± 82 nm, and a coating thickness of 64 ± 26 nm. Another copolymer often used to enhance the spinnability of collagen without toxic solvents is poly(L-lactide-co- ϵ -caprolactone) [221]. Zhong *et al.* [222] prepared collagen-glycosaminoglycan scaffolds through electrospinning in a mixture of TFE and water, followed by glutaraldehyde vapour crosslinking. The biostability of the smooth nanofibres with a mean diameter of 260 nm was improved. Although much work has been done on collagen in clinical applications, not much has been done on the application of the collagen in water treatment [219, 223]. However, Davis and Maffia [224] successfully prepared collagen from type 1 bovine for water treatment and sludge dewatering. The collagen showed good potential as a coagulant of colloidal solids.

5.5. Gelatin

Gelatin, similar to other naturally occurring polymers, is biocompatible, biodegradable and non-toxic [12]. It is derived from animal tissue such as skin, muscle and bone. Gelatin is subdivided into Type A and Type B, depending on the extraction and chemical treatment. Gelatin type A is obtained from the acidic pre-treatment of collagen, whereas Type B is from alkali pre-treatment. The glutamine and asparagine are converted into glutamic and aspartic acid during alkali pre-treatment, yielding a high carboxylic acid content in gelatin Type B. Gelatin has been processed into various forms for a wide spectrum of applications such as food products, cosmetics and pharmaceuticals [225]. Although gelatin is readily soluble in water and polar solvents, the electrospinnability of gelatin is still a challenge. However, some reports indicated the possibility of electrospinning gelatin using solvents such as using 2,2,2-trifluoroethanol TFE [226], formic acid [66], and 1,1,1,3,3,3-hexafluoro-2-propanol (HIFP) [85]. Electrospinning gelatin in water can be done by applying heat above 37°C [220].

The use of copolymers is another conducive route, not only to electrospin gelatin, but also to improve the mechanical and chemical stability [85, 136]. Huang *et al.* [227] indicated that gelatin can be electrospun into smooth nanofibres with a diameter of 140 nm using 2,2,2-trifluoroethanol (TFE) as a solvent. With a concentration of 7.5 wt% of gelatin, the modulus was 117 MPa and the ultimate strength 4.9 MPa. Similar to collagen the gelation of gelatin and its sol-

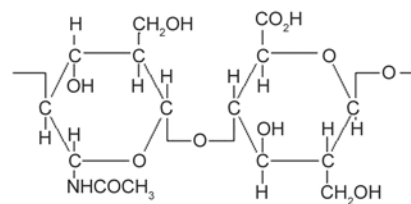


Figure 14. Structure of hyaluronic acid

ubility in water is the reason why it cannot be used in water treatment applications. The limitations of the application of gelatin are its weak mechanical strength and its ready solubility in water. The cross-linking of electrospun gelatin nanofibrous membrane is the most convenient way to improve the stability and mechanical strength [227].

5.6. Hyaluronic acid

Hyaluronic acid (HA), a natural polysaccharide, is often found in connective tissues in the body, such as the vitreous humour, the umbilical cord, and the joint fluid. It is a polyanionic acid made-up of N-acetyl-D-glucosamine and D-glucuronic repeating units as shown in Figure 14.

Thanks to the advancements in electrospinning, pure hyaluronic has been successfully electrospun into nanofibrous membrane from its solution [13, 15]. The electro-blowing of hyaluronic acid affords the preparation of its nanofibres with diameters ranging from 49 to 83 nm depending on the preparation and solution properties used. HA mats with an average fibre diameter of 39 ± 12 nm were produced from $\text{NH}_4\text{OH}:\text{DMF}$ at ratio 2:1 [228]. Many researchers studied the application of the hyaluronic acid in biomedical applications. The hyaluronic was immobilized on the surface of silica microspheres to fabricate a magnetic adsorbent. This shows the possibility to develop new adsorbents for wastewater treatment [229].

5.6.1. Hyaluronic acid with other biopolymers

Hyaluronic acid/chitosan electrospun bioblend nanofibres were prepared by Ma *et al.* [230] in a mixture of formic acid and water. Smooth fibres with smaller average diameters (83 nm) were obtained at higher contents of hyaluronic acid (hyaluronic/chitosan at 9/1), while at low contents beaded-fibres (7/3) and drops (6/4) formed.

5.6.2. Hyaluronic acid derivatives

A thiolated HA derivative, 3,3'-dithiobis(propionic dihydrazide)-modified HA (HA-DTPH), was syn-

thesized and electrospun into nanofibrous membrane by Ji *et al.* [86]. The dithiobis(propanoic dihydrazine) was synthesized and coupled to the carboxylic groups of HA via carbodiimide chemistry. The thiolated bond formed were reduced using dithiothreitol to produce thiolated HA-DTPH. HA-DTPH (2% w/v)/PEO (2% w/v) resulting in uniform nanofibres with diameters ranging from 70 to 110 nm. The resulting fibres were crosslinked with PGEDA (9 w/v), followed by the dissolution of PEO in deionized water for 48 hours. After the extraction of PEO the fibre diameter distribution became much wider (with 85% of the fibre diameters ranging between 50 and 300 nm). The crosslinking of the nanofibres reduced the swelling ratio of the mats. Another group investigated a similar system, but they used dual-syringe reactive electrospinning with thiolated HA/PEO into contact with PEGDA before electrospinning to induce crosslinking [86].

5.7. Aloe vera

Aloe vera is one of the oldest herbal products used for medicinal purposes. It contains more than 200 nutrients which include amino acids, salicylic acid, ascorbic acid, enzymes and lots of minerals and vitamins [231, 232]. It is largely made up of water with long chain polysaccharides of acetylated glucomannan and carbohydrates. So far there is no work based on the electrospinning of aloe vera alone, but blends of synthetic and biopolymers were used to facilitate its electrospinnability. We included aloe vera as biopolymer because of its biocidal efficacy (towards different pathogenic organisms), and the possibility to functionalize electrospun mats in water filtration and treatment to reduce the biofouling of the electrospun membrane. Nonetheless, aloe vera enjoyed its success over a wide array of medical applications [233].

5.7.1. Aloe Vera with synthetic/biopolymers

A hybrid of hydroxypropyl methylcellulose (HPMC), poly(vinyl alcohol) PVA, poly(vinyl pyrrolidone), iodine PVP and poly(ethylene glycol) (PEG) were doped with aloe vera to investigate the effect of aloe vera on the properties of the resulting nanofibrous membrane. Like any biopolymer, aloe vera influenced the solution properties such as viscosity and conductivity. The addition of aloe vera increased both the viscosity and conductivity of the spinning solution, and decreased the mean diameter of the ensuing nanofibres from 660 to 596 nm at 1% of aloe

vera. SEM showed an interfuse with each other when the content of aloe vera increased in the composition. In another study the addition of aloe vera (at 6%) resulted in finer and more homogeneous nanofibres with mean diameters of 150 to 350 nm [232]. A similar study on the hybrid of biodegradable PCL and aloe vera to prepare transdermal biomaterial showed homogeneity and small average diameters of the nanofibres in the presence of aloe vera (519 ± 28 versus 215 ± 63 nm at 10% aloe vera), and greatly improved mechanical properties and hydrophilicity [234].

6. Electrospun biopolymers with nanomaterials

In the past few years there has been an ever increasing interest in incorporating different nanoparticles in biopolymers for a broad range of applications [26, 235]. Nanoparticles have a promising potential in wastewater/water treatment as biocidal agents, sensors, and adsorbents. If these nanoparticles are used alone for water/wastewater treatment there are some limitations such as their recovery and reuse, cost and their long-term effect on health and/or the environment. The biocidal activities of these nanoparticles are depicted in Table 5. A possible solution is to immobilize and control their release to overcome these complications/limitations [236, 237]. Electrospinning these nanomaterials (with known content) with biopolymers offers the possibility to retain their nanosize and their release into streams without any harmful by-products, thus reducing the overall cost.

6.1. Silver nanoparticles

Silver is well-known for centuries for its attractive antimicrobial, antiviral and fungicidal activity [236, 238]. The metal enjoyed its success in a broad spectrum of consumer products, such as plastics, soaps, pastes, food and textiles. The antimicrobial and antifungal activity of silver nanoparticles (AgNP) makes it the most studied metal nanoparticle for different applications [234–236]. There are several ways by which ionic silver can be reduced into silver nanoparticles [26, 238]. There is still a lot of controversy on the mechanism behind the antibacterial, fungicidal, and antiviral activity displayed by silver nanoparticles. Three mechanisms were postulated, namely i) attachment of the silver nanoparticles on the surface of the cell membrane and disturbing its permeability and respiration, ii) penetrating the cell and

Table 5. Summary of common antibacterial nanomaterials and applications

Nanomaterial	Proposed antimicrobial mechanism	Potential water treatment applications
Silver (AgNP)	Release of Ag ⁺ ions, disruption of cell membrane and electron transport, DNA damage	Surface coatings, membranes, membrane reinforcement
Carbon nanotube (CNT)	Disruption of intracellular metabolic pathways, oxidative stress, physical membrane damage	Biofouling resistance membranes, carbon hollow fibres, membrane reinforcement
Hydroxyapatite (Hap)	Easy functionalization with different biocidal metal oxide	Membrane reinforcement
Zinc (ZnO)	Intracellular accumulation of nanoparticles, disruption of cell membrane, H ₂ O ₂ production, release of Zn ²⁺ ions	Surface coating, membranes, membrane reinforcement

reacting with some compounds containing sulphur and phosphorus such as DNA and proteins, and iii) releasing silver ions which contributes to its activity towards pathogens [236]. These mechanisms depend on the distribution, shape and size of the silver nanoparticles.

Formic acid was used as solvent to prepare chitosan/PVA nanofibres with optimal conditions of 0.5 mL·h⁻¹ flow rate, 18 kV voltage and a TCD of 7.5 cm. Chitosan/PVA was doped with silver oxides and titanium oxides to significantly improve the antibacterial activity of the ensuing nanofibres [26]. The prepared nanofibres with mean diameters ranging between 270 and 360 nm were cultured to find their antibacterial activity against both Gram negative and Gram positive bacteria. The antibacterial activity of AgNO₃ loaded composite nanofibres increased with an increase in AgNO₃ content with 99% bacteria eradicated for *S. aureus* and 98% for *Escherichia coli* at only 0.04 wt% of AgNO₃. TiO₂ loaded composite nanofibres showed a maximum of 90% bacteria for *S. aureus* and 85% bacteria for *Escherichia coli* eradicated at concentrations above 0.03 wt% of TiO₂.

The diameter of the nanofibres also influenced the antibacterial activity, with smaller diameters showing better efficiency because of the large surface to volume ratio giving more contact with the bacteria. A similar blend of chitosan and PVA was doped with AgNPs [239]. A 12 wt% PVA solution containing AgNO₃ blended with a 6 wt% chitosan solution (15 wt% in acetic acid) was electrospun, followed by either refluxing for 48 hours or annealing at 130°C for 16 hours (to reduce Ag ions of the nanofibres). The intensities of surface plasmon resonance (SPR) of AgNPs increased in the presence of chitosan compared to that of PVA and AgNO₃ only, indicating that chitosan can act as a stabilizer as well as a reducing agent for the formation of AgNPs. The spherical AgNPs on the surface of the electrospun nanofibrous membranes were fairly uniform and smaller in size when refluxed, while larger particles were asso-

ciated with diffusion and agglomeration of residual Ag ions and AgNPs formed in the solid during heating were formed when annealed. This resulted in a lower killing efficiency of the annealed samples due to the surface area of the AgNPs coming into contact with the bacteria.

An *et al.* [240] prepared chitosan (CS)/polyethylene oxide (PEO) containing AgNPs nanofibres by means of *in situ* chemical reduction of Ag ions. The average diameter of the nanofibres decreased with an increase in AgNPs because of the increased charge density in the spinning solution, imparting stretching of the electrified jet under the electrical field. The cubic crystal AgNPs were fairly well dispersed in the CS/PEO ultrafine nanofibres with average diameter of less than 5 nm. The tensile modulus and tensile strength of the CS/PEO/AgNP nanofibres were better than that of the CS/PEO nanofibres. The CS/PEO/AgNP nanofibrous membrane exhibited higher antibacterial activity than the CS/PEO nanofibres towards *E. coli*. Silver nanoparticles were also incorporated into PVA/CS blends for their antibacterial activity [241]. The electrospinnability of the PVA/CS was enhanced by the AgNPs, and the size of the AgNPs varied between 2.4 to 10.7 nm depending on the CS concentration in the blends. A biopolymer blend of CS/gelatin containing AgNPs was successfully electrospun by Zhuang *et al.* [242]. The study indicates that the microcrystalline chitosan was used as reducing agent and stabilizer to synthesize the AgNPs at room temperature. Using a noniogenic polymer (PEO), a natural polymer (N-carboxyethyl-chitosan), and silver nanoparticles, Penchev *et al.* [87] observed a complete killing of the bacteria (*Staphylococcus aureus*) within an hour of contact at higher concentrations of silver nanoparticles, whereas at low concentrations the nanoparticles only inhibits bacterial growth. They used a one pot system to fabricate the nanofibre in which all the components were added into the spinning solution. Formic acid was again used as reducing agent and solvent, and the

sizes of the NPs were 4 ± 0.5 and 6 ± 1.5 nm respectively for 5 and 10 wt% of the AgNO_3 . Yang *et al.* [31] fabricated antimicrobial membrane using cellulose acetate and AgNO_3 by slow and fast photoreduction. The mats were tested against *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumonia*, and *Pseudomonas aeruginosa* by an attachment method. The mean diameter of the ultrafine nanofibres ranged between 680 and 610 nm for 0.05 and 0.5 wt% of AgNO_3 , respectively. Most of the nanoparticles had a mean diameter between 3 and 16 nm, whereas 15.4 nm resulted after rapid photoreduction. The killing efficiency for all the bacteria was 99.9% at a very low concentration of 0.05 wt%. Lee *et al.* [243] produced electrospun chitosan nanofibres with chemically reduced AgNPs via electrospinning. The resulting spherical nanoparticles with sizes ranging between 10 and 11 nm (average diameter of 10 ± 2 nm) were evenly distributed in the chitosan nanofibres. The growth inhibition of *Pseudomonas aeruginosa* (gram negative) and *Staphylococcus aureus* (gram positive) increased with an increase in AgNPs in the composite materials.

6.2. Hydroxyapatite (HAp) nanoparticles

Celebi *et al.* [244] produced electrospun chitosan/PVA nanofibrous membrane containing silver ion-incorporated hydroxyapatite (HAp) nanoparticles. A mean diameter of ~ 70 nm of silver ions-incorporated HAp particles were obtained with good antibacterial efficiency against *Escherichia coli*. Hydroxyapatite (HAp)/chitosan was synthesized by co-precipitation synthesis followed by electrospinning of 10 wt% UHMPEO in aqueous solution with the solvent composed of acetic acid (HAc) and dimethyl sulphoxide (DMSO). The X-ray diffraction (XRD) and selected area electron diffraction (SAED) spectra confirmed that the crystalline structure of HAp was retained in the nanofibres [217]. The electrospun nanocomposite nanofibrous membrane were finer and more homogeneous with diameters of 214 ± 25 nm with spindle-like HAp parallel to the nanofibres direction. A similar dispersion of HAp and structure were reported using gelatin as matrix [245]. The mechanical properties were also improved in the presence of HAp.

6.3. Carbon nanotubes

Carbon nanotubes have excellent antimicrobial activity and mechanical strength. Similar to Ag nanopar-

ticles, the mechanism of the carbon nanotubes against pathogenic organisms is still controversial [236]. The proposed mechanisms include physical membrane perturbation and oxidative stress. Their antimicrobial activity is also influenced by their distribution, diameter, length, and electronic structure. Most of the carbon nanotubes exhibit good cytotoxicity towards pathogenic organisms, with single-walled carbon nanotubes reported to be the most efficient. Well-aligned single walled carbon nanotube (SWNT) along the fibre axis of the *bombyx mori* silk nanofibre were produced by Ayutsede *et al.* [246]. A very low concentration of SWNT (1 wt%) was enough to increase the crystallinity and mechanical properties. Multiwalled carbon nanotubes (MWNTs) were also incorporated in electrospun cellulose acetate (CA) nanofibres to investigate the effect of these nanoparticles on biopolymers [247]. The mean diameter of the nanofibres reduced from 267 nm for pure CA to 193 nm with MWNTs at only 0.55 wt%. The MWNTs impart significant water wetting, surface area (from 4.3 to 7.7 $\text{m}^2\cdot\text{g}^{-1}$), Young's modulus (doubled from 553 to 1144 MPa), tensile strength (from 21.9 to 40.7 MPa) and elongation at break (from 8.0 to 10.5%). A core-sheath structure of PVA/CS-MWNT with outer and inner sheath-core nanofibres of 200 and 100 nm respectively was reported by Feng *et al.* [248]. The composite nanofibres showed fast transfer kinetics and good electrochemical properties. In one of their recent studies on electrospun silk fibroin (*B. mori*)/multiwalled carbon nanotubes they reported that MWNTs induced crystallization of silk and significantly improved the mechanical properties [249].

6.4. Zinc nanoparticles

Zinc nanoparticles (ZnO) antibacterial activity is still not clear, but several mechanisms were proposed. It was suggested that the lethal effect of ZnO results from disruption of the cell membrane activity and induction of intercellular reactive oxygen species, such as H_2O_2 , a strong oxidizing agent harmful to bacterial cells [236]. Zinc oxide was produced by mixing the precursor (zinc acetate) in 0.1 M sodium hydroxide in methanol [250]. The prepared ZnO was introduced in an alginate/PVA blend dissolved in distilled water. With a large contact area the composite exhibited high toxicity to both gram-negative and gram-positive bacteria. Taha *et al.* [156] functionalized a cellulose acetate/silica composite with NH_2 to enhance its affinity towards Cr(IV) ions. They used

tetraethoxysilane (TEOS) as silica source, cellulose acetate as precursor and 3-ureidopropyltriethoxysilane as a compatibilizer. They produced NH_2 functionalized nanofibres with a mean diameter of 100–500 nm and a porosity and surface area of 73% and $126.5 \text{ m}^2\cdot\text{g}^{-1}$. Using static and dynamic experiments the membrane showed adsorption of 98%. ZnO nanoparticles were impregnated into the electrospun cellulose acetate nanofibre membrane by Anitha *et al.* [251]. The membrane displayed a superhydrophobic nature (water contact angle of 124°) and antibacterial property against well-known bacteria.

7. Applications of electrospun biopolymers in water treatment

Electrospun nanofibres afford the opportunity to be applied in various fields such as biosensors, and filtration because of their unique properties such as large surface area and engineered porosity, and physico-mechanical properties. The manipulation of the solution properties and technique advancement rendered the opportunity to produce the desired morphology and structure of the resulting nanofibres for specific applications.

7.1. Bioremediation

Heavy metals in wastewater is still a big problem, and a challenge to researchers to come up with reliable solutions without leaving by-products. Cellulose acetate has been functionalized to increase its adsorption efficiency which depends mostly on the functional groups found on the main chain. Poly(methacrylic acid) (PMAA) with additional carboxyl groups was used to functionalize cellulose acetate to increase the number of metal binding sites [252]. The efficiency was enhanced by the presence of PMAA on the cellulose acetate fibres, but the adsorption was more effective for the removal of mercury (Hg(II)) with an adsorption capacity of $4.8 \text{ mg}\cdot\text{g}^{-1}$. The efficiency may, however, depend on the metal ion type and the pH. The de-adsorption of the metals is possible with an appropriate solvent such as ethylenedinitrilotetraacetic acid (EDTA). Cellulose acetate/silica composites were tested for Cr(VI) adsorption [156]. In this case the CA/SiO_2 was functionalized with NH_2 to enhance the adsorption of the resulting fibre membranes. The membranes displayed a good adsorption, and desorption after washing five times with an aqueous solution of sodium hydroxide (NaOH). The adsorption data of Cr(VI) fitted well

with the Langmuir isotherm with an adsorption capacity of $19.5 \text{ mg}\cdot\text{g}^{-1}$.

Although various mechanisms were proposed to describe the metal ions adsorption of chitosan, the electrostatic attraction on the protonated amine groups is the accepted mechanism [253]. The heavy metal adsorption efficiency of an electrospun chitosan membrane was studied by several researchers [10, 254]. It was found to depend on several aspects such as the degree of deacetylation [254], pH, fibre structure and morphology [181, 254]. Desai *et al.* [254] studied the adsorption efficiency of PEO/chitosan nanofibres electrospun towards chromium using simulated flow conditions at a pH of 7.3. The chromium solution (prepared from $5 \text{ mg}\cdot\text{L}^{-1} \text{ K}_2\text{CrO}_4$) was passed ten consecutive times through the chitosan nanofibrous filter. The binding efficiency of the membrane decreased with an increase in nanofibre diameter (81–131 nm). However, the heavy metal adsorption efficiency increased with an increase in the degree of deacetylation. Using static conditions, the same group found that the metal adsorption depends on the molecular weight of chitosan, the degree of deacetylation, the percentage of chitosan in the blend, and the surface area to mass ratio. The molecular weight is related to the length of the chains and therefore to the number of cations on the backbone of the chitosan acting as active binding sites.

Cho *et al.* [10] neutralized the nanofibres with K_2CO_3 to obtain an $-\text{NH}_2$ group on the backbone of the chitosan membrane. This improved the stability of the electrospun membrane in water, with negligible weight reduction after 24 hours. The adsorption of the metals (Cu(II) , $419.2 \text{ mg}\cdot\text{g}^{-1}$ and Pb(II) , $202.8 \text{ mg}\cdot\text{g}^{-1}$) increased significantly for the first 15 min to 4 hours and levelled off after 8 hours, due to the unavailability of binding sites (amine, primary and secondary hydroxyl groups), large surface area, and inter- and intrafibrous pores in the fibrous membrane. The Langmuir isotherm data showed that the equilibrium adsorption capacities for Cu(II) and Pb(II) were respectively $485.4 \text{ mg}\cdot\text{g}^{-1}$ ($2.85 \text{ mmol}\cdot\text{g}^{-1}$) and $263.2 \text{ mg}\cdot\text{g}^{-1}$ ($0.79 \text{ mmol}\cdot\text{g}^{-1}$). The difference between the values for the two metals was attributed to the differences in their atomic radii. It was suggested that the chitosan' adsorption followed a monolayer mechanism.

A nanofibrous membrane of pure silk fibroin (SF), and a blend of wool keratose and silk fibroin

(WK/SF), were compared with pure silver wool and filter paper for their Cu(II) adsorption capacity [255]. The nanofibrous membranes displayed a significant Cu(II) adsorption capacity compared to silver wool and filter paper because of the large specific area which is ~50 times larger than those of filter paper and silver wool. The blend membrane showed a higher capacity than the SF membrane. The difference in Cu(II) adsorption capacity was related to the different chemical compositions (especially amino acids compositions). Both membranes displayed good desorption percentages. Desorption and re-adsorption was repeated six times, but the membrane kept 90% of its adsorption capacity. The Langmuir isotherm fits the experimental results better than the Freundlich model. The Cu(II) adsorption followed a monolayer adsorption model.

Yang *et al.* [256] functionalized oxidized cellulose nanofibres embedded in an electrospun polyacrylonitrile (PAN) nanofibrous membrane with thiol groups to evaluate the metal adsorption capacity. Besides the increased stiffness due to the functionalization, the functionalized composite membrane displayed an adsorption of $76.5 \pm 2.0 \text{ Cr}_2\text{O}_7^{2-}$ metal ions per gram of cellulose nanofibre at pH = 4.0, while the adsorption of Pb(II) was $133 \pm 2.5 \text{ mg} \cdot \text{g}^{-1}$ at pH = 5 in static conditions. The membrane also reached $80.0 \text{ mg} \cdot \text{g}^{-1}$ of Pb(II) within 15 minutes, and $125 \text{ mg} \cdot \text{g}^{-1}$ within 20 minutes. Under dynamic conditions the membrane showed 60 mg Cr(VI) g^{-1} (pH = 4) and 115 mg Pb(II) g^{-1} were adsorbed. Wang *et al.* [257] grafted cellulose nanowhiskers with amine groups using polyvinylamine (PVAm). The membrane displayed a maximum dynamic adsorption of 100 mg Cr(VI) (at pH = 4) and 260 mg Pb(II) (at a pH of 6) per gram of cellulose nanofibre.

7.2. Filtration membrane

Even though electrospun nanofibrous membranes were successful in air filtration, much work was still needed for water filtration. The breakthrough came when the electrospun nanofibres were spun onto more rigid nonwoven polyesters to improve handling issues and their mechanical properties [29]. The thin composite membrane (TNFC) significantly enhanced the rejection and flux permeation of the membranes, because of the nanofibres with high porosity and controllable pore size for specific filtration processes. TNFC membranes have been one of the growing subjects in water filtration, because of

the performance displayed by these materials since the introduction of electrospun nanofibres as one of the sub-layers.

Several researchers found that the coating of these TNFC with cellulose nanowhiskers imparts significant hydrophilicity and mechanical properties to the membrane [144, 149–152]. The thin top-layer coating enhanced the rejection and flux. Wang *et al.* [258] found that the interfacial polymerization of polyamide around the ultrafine cellulose nanofibres layer in TFNC showed a good rejection of MgCl and MgSO_4 , depending on the adapted interfacial polymerization (i.e. IP, the organic phase on top of the aqueous phase, or IP-R, the aqueous phase on top of the organic phase). The IP based membrane showed a rejection of 67.6% at 1% of piperazine (PIP), while the IP-R showed a rejection of 91.6% of MgSO_4 . However, both membranes displayed similar rejection percentages for both MgSO_4 and MgCl at higher PIP concentrations. The same group electrospun PAN onto PET and infused cellulose nanowhiskers (diameter 5 nm) for the microfiltration process [257]. The cellulose nanowhiskers were functionalized with different amines such as polyethyleneimine (PEI), ethylenediamine (EA), and polyvinylamine (PVAm) by using N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) and N-Hydroxysuccinimide (NHS) as catalysts. The resulting cellulose-based membrane had a mean pore size of $0.38 \mu\text{m}$ with a maximum pore size of $0.78 \mu\text{m}$, and the water permeation was about $1300 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{psi}^{-1}$. All the membranes showed complete removal of the bacteria by size exclusion. The coating of chitosan on electrospun PAN enhanced the filtration efficiency and rejection for both ultrafiltration and nanofiltration processes [259]. The membrane displayed a rejection of 99% due to the inherited hydrophilicity of chitosan.

7.3. Biocidal membrane

Biofouling is a major problem for most membranes, because it results in the accumulation and biological growth of pathogenic organisms, and the deterioration of the membrane performance. A variety of metal oxides have been added to the electrospun biopolymer nanofibres to impart biocidal activity to the resulting nanofibres. Most of the diseases in developing countries are caused by pathogenic organisms. There has been an escalation of research in incorporating silver nanoparticles in the electro-

spun membrane to impart biocidal activity [156, 239, 240, 243, 244]. Even though there is still much controversy over the biocidal activity of the silver nanoparticles, electrospun nanofibres displayed enhanced antibacterial efficiency when the membranes contained silver. ZnO particles were introduced in an alginate/PVA blend dissolved in distilled water, followed by electrospinning [250]. With the high contact area the electrospun composite displayed toxicity to both negative and positive bacteria. ZnO nanoparticles were also incorporated in a cellulose acetate membrane to enhance the antibacterial efficiency against *Staphylococcus aureus*, *E. coli*, and *Citrobacter freundii*. [251]. The impregnated ZnO nanoparticles significantly inhibited the growth of the bacteria and the inhibition zone diameters were 27, 22, and 14 mm for *Staphylococcus aureus*, *Escherichia coli*, and *Citrobacter freundii*. The functionalization of the electrospun membrane also enhanced the biocidal efficiency [83, 193, 195]. A quaternized chitosan membrane displayed inhibition of bacterial growth on the mat. Blending biopolymers with good antibacterial efficiency was also significantly reduced the biocidal activity of the resulting membrane [83].

7.4. Chemosensors

Chemosensors are detectors to selectively identify and recognize ions and molecules. A number of studies have been done on implanting the chemosensing agent onto solid matrices to improve the sensitivity, robustness, and lifetime [260]. A variety of polymers and nanomaterials were used as supporting materials in solid-state sensors. The sensitivity detection and exposure of the chemosensors was found to be directly dependent on the structure of the supporting material [261].

The sensing agent embedded onto electrospun nanofibres (with large surface areas) improves the detection sensitivity and response time, and reduces the concentration detection value (lowest detection value (LOD)) compared to commonly used films. The presence and concentration of the heavy metals can therefore be traced and removed at fairly low concentrations. Several biobased nanofibres such as ethyl acetate, cellulose acetate and cellulose have been functionalized with different fluorescent compounds to detect Cu [260–262]; Cr [260], Fe [263] and Hg ions [261, 264]. Due to the large surface areas of the electrospun nanofibres, the sensitivity, selectivity,

response time, and stability were enhanced. Kacmaz et al. [263] produced electrospun EC doped with dye to detect Fe^{3+} ions. The membrane sensed Fe^{3+} ions over a concentration range of 10^{-12} – 10^{-6} M (with an LOD of 0.07 pM), with a sensitivity response time of less than 30 s and sensor regeneration within 60 s.

Zdyrko [265] developed a self-deployable colorimetric sensor by taking advantage of the super-absorbency of alginate, and functionalizing it with a heavy metal sensitive compound/dye. A blend of alginate and PEO electrospun onto rigid nonwoven (PET) absorbed metal ions from contaminated water.

8. Limitations of electrospun biopolymers in water treatment

Besides the hurdles based on the production scale-up of biopolymers, properties from the same source differ and the growth conditions influence the resulting properties. The harsh chemical treatment used to extract some biopolymers put an additional burden onto the water and the environment. It is important to do a lot of research on genetically engineering organisms and novel designed productions to scale up the production of biopolymers with high purity/quality and having identical properties. Electrospun nanofibrous membranes have limited mechanical strength to withstand the pressures involved in water filtration, thus they are only applicable in membrane technologies where low pressures are involved (MF, UF and NF). Even though the work done on electrospun biopolymers shows potential to use eco-friendlier solvents, their application in water/wastewater treatment is still in its infancy. Most of these polymers are naturally prone to biodegradation and some are readily soluble in water, hence their lifetime is too short and they will need to be regularly replaced over time. This results in increasing the price of the membrane. The enhancement of the stability via either chemical or physical treatment without altering the unique valuable properties of the bio-based membranes is important for their application in water/wastewater treatment. The dispersion of the nanomaterials in electrospun nanofibres (without agglomeration to retain their nanosize), and their exposure and release into the stream requires a lot of understanding. Most methods used to prepare the electrospun composite materials revolve around coating the mat (immersing the mat in a metal oxide

solution) or adding the nanomaterial into the spinning solution. Nanomaterials from these methods have different release rates and exposure to the water stream. In the near future, investigation of the controlled release and exposure of the nanomaterials is required to understand and control their disinfection efficiency.

9. Conclusions

In the past decades, electrospinning has been highly recognized as a new class of nanotechnology providing access to a range of nanomaterials with unique properties. Significant progress has been made on the fundamental understanding of the mechanism, and the modelling of the envisaged processes governing the fibre formation. This was proven by advanced developments to engineer desired nanostructured materials through electric field manipulation, solution properties and new designs. Control over their deposition, dimensions and assemblies created new avenues to generate desired configurations for specific applications. There is currently a big paradigm shift towards the industrialization and commercialization of the electrospun nanofibres. The new technical advances (fibre collections strategies, needle shapes, and high throughput production) proved to

be successful in the synthesis of these fascinating nanostructured materials. A fair amount of work has been done on electrospinning biopolymers for a broad array of applications, especially in the biomedical field. Much of this work was based on electrospinning of biopolymers with and without copolymers and using non-toxic solvents. Water filtration and wastewater treatment received little attention, despite the unique properties of biopolymers that are important in addressing environmental concerns. The biodegradation and mechanical strength of the electrospun mats are critical limitations in water filtration and wastewater treatment. In future the mutual relation to protect and improve the strength of the electrospun biopolymers by blending, chemical and physical treatment, and the addition of metal oxides and their controlled release into water streams will revolutionize wastewater treatment and water filtration. Through further research it will be possible to bridge the gap to enable the application of biopolymers in water filtration and treatment.

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Abbreviations

3D	three dimensional
AgNP	silver nanoparticles
C	concentration
CA	cellulose acetate
CMC	carbomethyl chitin
CMCs	carboxymethyl cellulose sodium salt
CoPc	cobalt tetraaminophthalocyanine
CV	crystal violet
D	diameter
DCM	dichloromethane
DD	deacetylation degree
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DNA	deoxyribonucleic acid
DOSE	dual-opposite-spinneret electrospinning
DS	Degree of substitution
EA	ethylenediamine
EC	ethyl cellulose
EDC	N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride
EDS	energy-dispersive X-ray spectroscopy
EDTA	ethylenediaminetetraacetic acid
ENM	electrospun nanofibrous membrane
GAG	glycosaminoglycan
GJF	gas jet nanofibre

HA	hyaluronic acid
HA-DTPH	3,3'-dithiobis(propanoic dihydrazide)-modified hyaluronic acid
HAp	hydroxyapatite
HFIP/HFP	1,1,1,3,3,3-hexafluoro-2-propanol
HPMC	hydroxypropyl methyl cellulose
HTACC	N-(2-hydroxypropyl)-3-trimethyl ammonium chitosan chloride
LOD	lowest detection value
MeOH	methanol
MF	microfiltration
Mw	molecular weight
MWNT	multiwalled carbon nanotube
NHS	N-Hydroxysuccinimide
NMMO	N-methylmorpholine-N-oxide
NP	nanoparticles
P(CLLA)	poly(L-lactide-co-caprolactone)
P(LLA-CL)	poly (L-lactide-co-caprolactone)
PAA	polyacrylic acid
PAAm	poly(acrylamide)
PAN	poly(acrylonitrile)
PBS	phosphate buffered saline
PCL	polycaprolactone
PCLDLLA	poly(ϵ -caprolactone-co-D-L-lactide)
PEG	poly(ethylene glycol)

PEGDA	poly(ethylene glycol) diacrylate
PEI	polyethyleneimine
PEO	poly(ethylene oxide)
PES	poly(ether sulphone)
PET	poly(ethylene terephthalate)
PF	paraformaldehyde
PGA	poly(glycolic acid)
PIP	piperazine
PLA	poly(lactic acid)
PMAA	poly(methacrylic acid)
PS	polystyrene
PU	poly urethane
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
PVAm	polyvinylamine
PVDF	poly(vinylidene fluoride)
PVP	poly(vinyl pyrrolidone)
QBzCSN	N-benzyl-N,N-dimethyl chitosan iodide
QCh	quaternized chitosan
RJS	rotary-jet spinning
RNA	ribonucleic acid
SEM	scanning electron microscopy
SF	silk fibroin
SNE	standard electrospinning
SO ₃ H	sulphonate groups
SWNT	single walled carbon nanotube
TCD	tip-to-collector distance
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidioxo
TFA	trifluoroacetic acid
TFE	trifluoroethanol
T _g	glass transition temperature
T _m	melting temperature
TMP	trans-membrane pressure
TNFC	thin film composite membrane
TPU	thermoplastic polyurethane
UF	ultrafiltration
WK	wool keratose
XPS	X-ray photoelectron spectroscopy

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